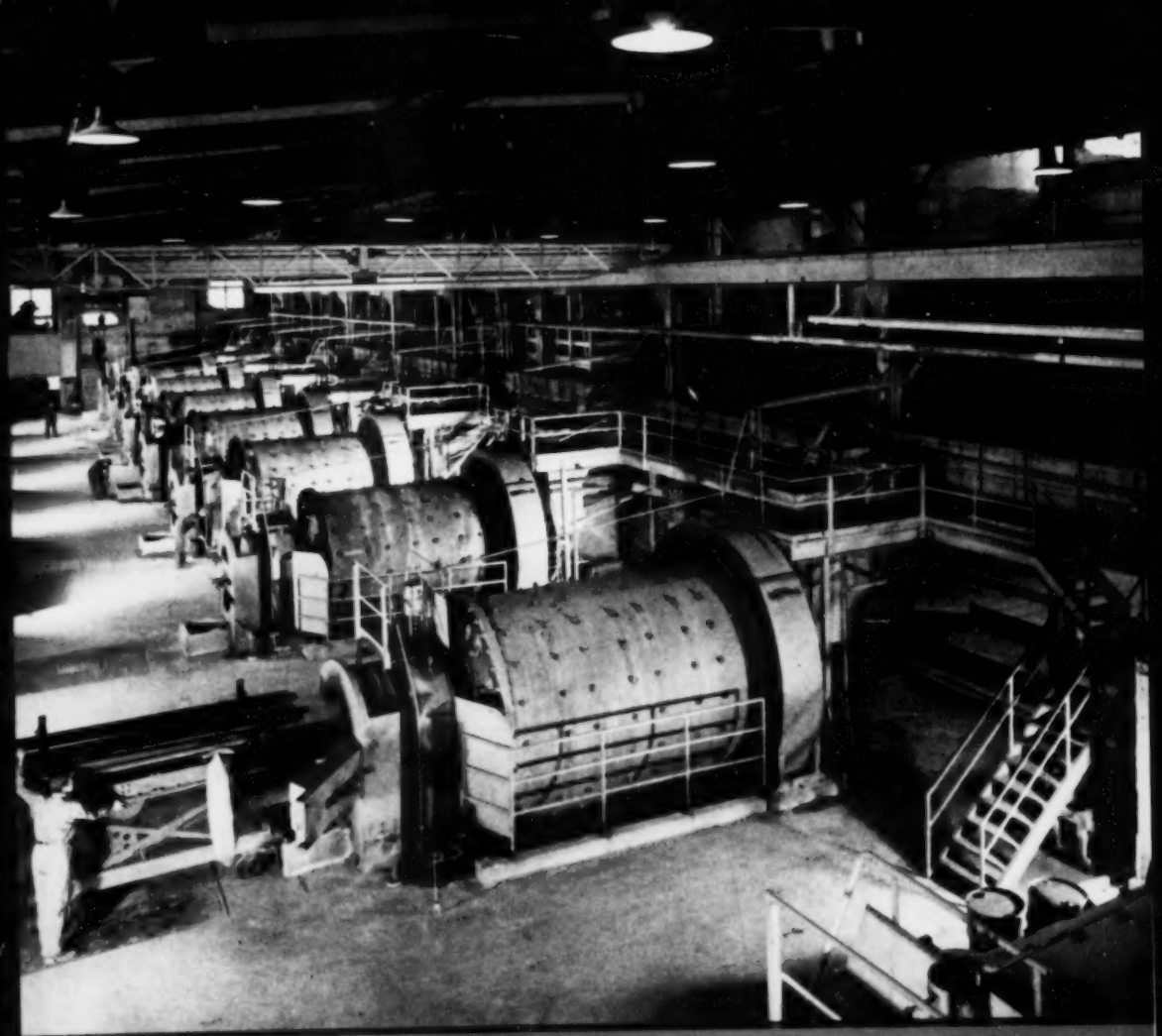
SEPTEMBER, 1952

Journal of METALS



September JOURNAL OF METALS Highlights:

"Operations At Monterrey Lead Refinery" - p. 915
"Instrumentation Improves Steel Mill Production" - p. 919
"Use of Oxygen In The Bessemer Converter" - p. 933

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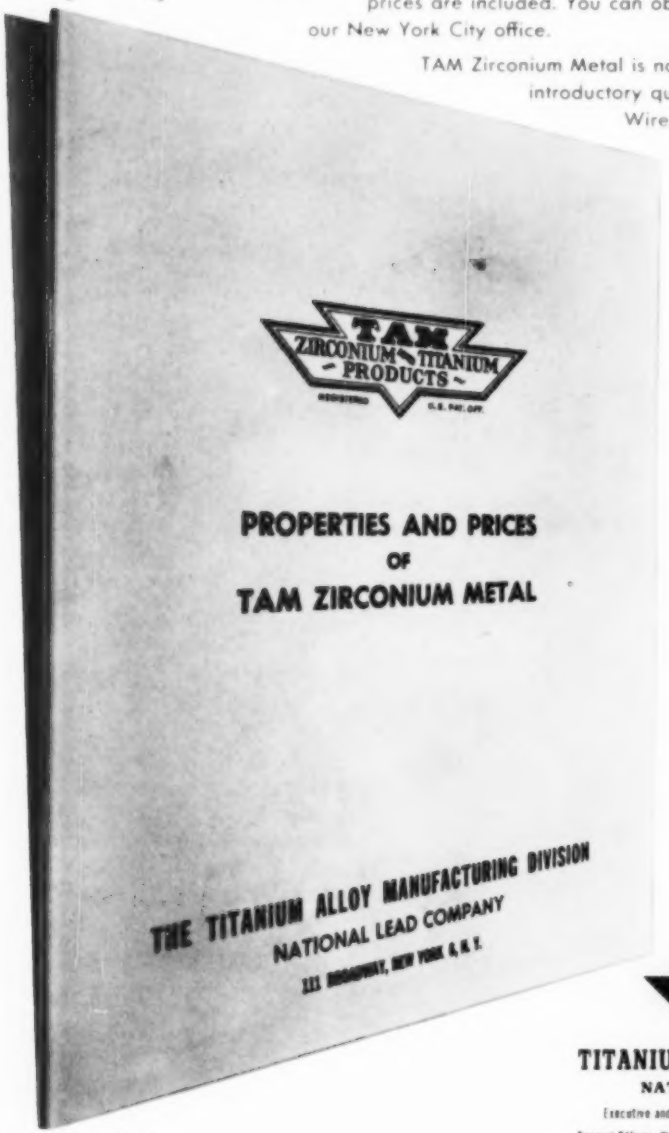

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VOL. 4, NO. 9 SEPTEMBER, 1952

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COVER

This battery of eight new rod mills represents part of the $31½ million being used for new copper processing equipment in the concentrator at Anaconda, Mont. These mills are currently grinding over 6000 tons of ore per day, and are capable of grinding the entire 15,000 tons per day, which is the production target for the Greater Butte Project.

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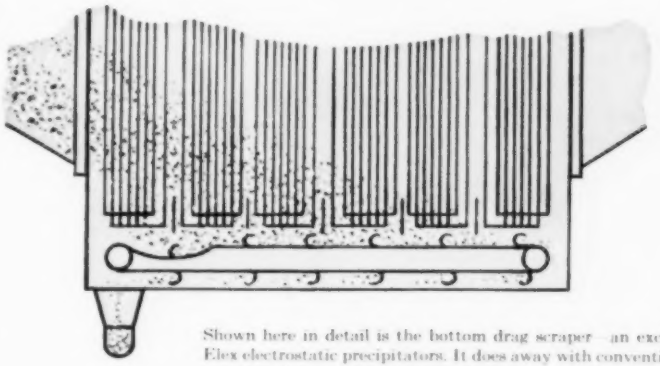

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MEET THE AUTHORS

W. T. Rogers (p. 933) has been associated with the National Tube div. of U. S. Steel Co. since 1923. He is now statistical engineer at the Lorain, Ohio works. Mr. Rogers joined the firm as a mill worker and has been metallurgical observer, statistical clerk, student engineer, and statistical engineer, respectively. He has authored several papers on the subject of statistical quality control and has lectured widely on the subject.

David Moskowitz (p. 963), a resident of Bronx, N. Y., is a graduate of City College of New York (B.S.) in 1949. Mr. Moskowitz has been associated with the American Electro Metal Corp., Yonkers since 1951 and is presently physical research assistant. In his spare moments he enjoys listening to his collection of records.

W. T. ROGERS

D. MOSKOWITZ

J. P. Morris (p. 939) received his B.S. from the University of Arkansas in 1935 and received his M.S. in 1936. Since 1947 he has been employed as a chemist at the Bureau of Mines, Pittsburgh. He is engaged in research on analytical procedures and equilibria in high temperature metallurgical reactions. *Effect of Carbon on the Activity of Sulphur in Liquid Iron* is the title of a paper previously presented.

L. B. Ticknor (p. 941) is a staff member at the div. of industrial cooperation, Massachusetts Institute of Technology. Dr. Ticknor was born in Centralia, Wash. and received his B.S. and Ph.D. degrees in physical chemistry from M.I.T. Now residing at Dedham, Mass. he enjoys mountain climbing and square dancing in his free time.

J. P. MORRIS

L. B. TICKNOR

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S. F. Reiter (p. 972) was born in New York. He received his B.ME. (1947) from Cornell, M.Eng. (1947) and D.Eng. (1951) from Yale. During World War II, Dr. Reiter served with the Navy. He joined the engineering dept. of the Chase Brass & Copper Co., Waterbury, Conn. in 1947. At present he is a research associate at the General Electric Co. research laboratory, the Knolls, Schenectady. A member of the AIME New York Section, he also holds membership in the ASME and ASM. Skiing, riding, and painting occupy Dr. Reiter in his free time.

Suzanne E. A. Beatty (p. 987), born in Yonkers, N. Y., is a graduate of Wellesley, B.A. and University of Michigan, Ph.D. For one year she was a National Research Fellow at the Mt. Wilson Observatory. In 1947 Mrs. Beatty joined the Westinghouse Research Laboratories, Pittsburgh as a research chemist. Now residing in Arcadia, Calif., she likes traveling, mountain climbing, skiing, and tennis.

S. F. REITER

S. E. A. BEATTY

Oleg D. Sherby (p. 939), graduate of the University of California, B.S. and M.S., was born in Shanghai, China. In 1949 Mr. Sherby joined the staff of the Institute of Engineering Research at the University of California as research engineer. He is a member of the San Francisco Section, AIME, ASM, and Society of Rheology. *The Effect of Alloying Elements on the Elevated Temperature Plastic Properties of Alpha Solid Solutions of Aluminum* is the title of a paper he previously presented. Now residing in Albany, Calif., he enjoys tennis, skiing, and camping.

M. B. Bever (p. 941) graduated from Massachusetts Institute of Technology in 1944 (Sc.D.). He has been engaged in study, teaching, and research since 1938 and in 1948 he was appointed associate professor. Now residing at Cambridge, Dr. Bever is a member of the Boston Section of AIME. He has presented various papers before AIME and is also a member of the Institute of Metals. Hiking and skiing are his hobbies.

M. B. BEVER

O. D. SHERBY

Robert Steinitz (p. 933) was born in Beuthen, Germany. Dr. Steinitz graduated from the Institute of Technology, Charlottenburg and the University of Goettingen, Germany. In 1933 he was employed by Fred Krupp AG and a few years later came to the United States. He joined the Crucible Steel Co., Harrison, N. J. and in 1940 became associated with the American Electro Metal Corp., where he is presently employed. A member of AIME, he presented the paper entitled *Magnetic Properties of Iron-Powder Compacts*.

L. T. Sanchez (p. 933) is superintendent of the Bessemer dept., National Tube div., U. S. Steel Co., Lorain, Ohio. Born in San Juan, Mr. Sanchez is a graduate of Holy Cross College (B.S.) and Massachusetts Institute of Technology (M.Sc.). He has held the positions of open hearth metallurgist and open hearth melter with U. S. Steel Co. Among his hobbies, Mr. Sanchez counts stamp collecting and horseback riding.

R. STEINITZ

L. T. SANCHEZ

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A. E. White (p. 946), born in Plainville, Mass., is a graduate of Brown University and Harvard. In 1908 he was head of research for the Jones & Laughlin Steel Co. Professor White joined the staff of the University of Michigan in 1911 and is now professor of metallurgy and director of the dept. of engineering research. He is also a consulting engineer for the Detroit Edison Co., Philadelphia Electric Co., New England Power Co., and several other firms. Dr. White is a member of the AIME Detroit Section and has been past manager, ASME, past president, ASTM and ASM. In his spare time Dr. White enjoys photography.

E. E. Reynolds (p. 946) has been metallurgist in the research laboratory, Allegheny Ludlum Steel Corp., Watervliet, N. Y., since 1950. Born in Utica, Ohio, Dr. Reynolds attended the University of Michigan. He received his B.S.E. in 1944, M.S. in 1946, and Ph.D. in 1950. Prior to joining Allegheny Ludlum he had been a research engineer at the University in the engineering research institute. Dr. Reynolds is a member of the Metals Branch of the Institute, ASM, and Albany Society of Engineers.

A. E. WHITE

E. E. REYNOLDS

John E. Dorn (p. 959) is at present professor of physical metallurgy at the University of California. Dr. Dorn was born in Chicago and received his B.S. and M.S. degrees from Northwestern University and his doctorate from the University of Minnesota. From 1936 to 1938 he was a research associate at Battelle Memorial Institute. He joined the staff at the University of California in 1938 as an assistant professor. For one year Dr. Dorn was research metallurgist for the Dow Chemical Co., Midland, Mich., and in 1942 returned to the university as assistant professor, becoming an associate in 1946 and a full professor in 1948. He has presented several papers before AIME previously. Gardening and stamp collecting are enjoyed by Dr. Dorn in his free moments.

Italo S. Servi (p. 965) is now a research metallurgist at the research laboratories of Union Carbide & Carbon Corp., Niagara Falls, N. Y. Born in Gallarate, Italy, he holds S.M. and Sc.D. degrees. Before joining UCC he had been research assistant at Massachusetts Institute of Technology. In his free time, Dr. Servi enjoys photography and sketching.

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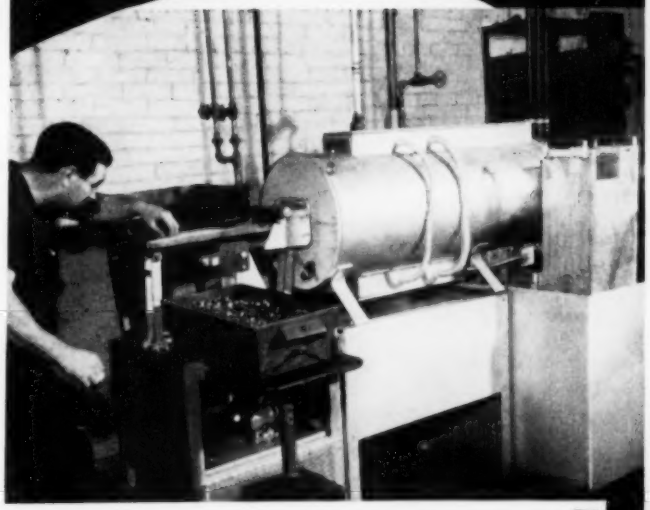

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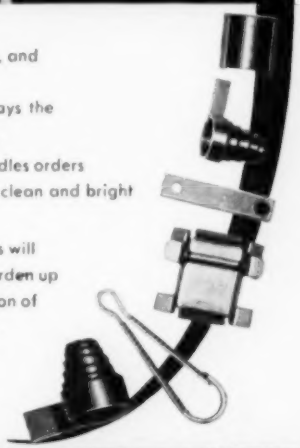

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Metallurgical Engineer with extensive plant design experience, to take charge of design of antimony oxidation and reduction plant. Location, Pennsylvania. Y7313.

Research Assistant, minimum requirement B.S. in metallurgy, chemistry or physics. Metallography, mechanical testing, statistical studies, interpretation of data, writing of technical reports and papers. Opportunity for tuition-free advanced study and for publishing technical material. One month's vacation. Apply by letter giving qualifications and salary expected. Location, western Pennsylvania. Y7172.

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Lead Smelter Engineer familiar with the blast furnace operations and subsequent refining and alloying processes, for a lead smelter operation based on the melting of battery lead scrap. Location, New York. Y6778.

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ELECTROMET *Data Sheet*

A Digest of the Production, Properties, and Uses of Steels and Other Metals

Published by Electro Metallurgical Company, a Division of Union Carbide and Carbon Corporation, 30 East 42nd Street, New York 17, N. Y. • In Canada: Electro Metallurgical Company of Canada, Limited, Welland, Ontario

High-Chromium, High-Carbon Iron

. . . the Iron That Hardens as it Wears

In many applications involving extreme abrasion, ordinary work-hardening alloys are not suitable. This is because most of these alloys require a definite pounding action for a martensite transformation, and the scouring action of an abrasive is not sufficient for development of high wear resistance. For this reason, high-chromium, high-carbon irons were developed — irons that wear harden.

Chromium Content of Irons Ranges from 24 to 30 Per Cent

These irons are made in the electric furnace and have the following composition range:

Chromium	26 to 28 per cent
Carbon	2.60 to 2.80 per cent
Manganese	0.50 to 1.25 per cent
Silicon	0.25 to 0.75 per cent
Sulphur	max. 0.05 per cent
Phosphorus	max. 0.05 per cent
Nickel	minimum
Iron	balance

Irons of this composition are readily castable by steel casting techniques.

Development of Greater Wear Resistance by Heat Treatment

Structurally, these irons consist of primary iron-chromium carbides in a matrix of iron-chromium solid solution and secondary iron-chromium carbides. They are hard in the as-cast condition (500 to 550 Brinell), but when they are given an austenitization heat treatment they develop much higher hardness (about 600 Brinell), and also have greatly improved wear resistance. Austenitization consists of heating these irons to a temperature of about 2012 deg. F. for an hour, then allowing them to cool in air. This heat treatment promotes the formation of very unstable austenite—austenite that will transform to a harder martensitic end-product even under rubbing or mild impingement action. Austenitization has been found to be far more effective in increasing wear resistance than the promotion of unstable austenite by the addition of ferrite-forming alloying elements.

High-chromium, high-carbon irons can also be annealed to sufficiently low-hardness values for grinding or simple machining. Hardnesses as low as 350 to 450 Brinell can be obtained by heating the castings to temperatures of 1400 to 1450 deg. F. for 12 to 24 hours, then allowing them to cool in air.

Irons Have Wear Resistance Many Times That of Other Alloys

Austenitized high-chromium irons have been known to last as much as 21 times longer than other wear-resistant alloys in applications involving extreme frictional abrasion. These applications include sand-blast nozzles and liners, pantograph contact shoes, grinding disks, pulleys, chute-liner plates, dredge-pump liners, and rollers for crushing various hard materials.

In a recent test, high-chromium iron was compared to special wear-resistant steel castings as the material for hammers in a machine that was used to crush abrasive material. The chrome-iron hammers were found to have almost 7 times the wear resistance of the steel castings.

Fig. 1. After crushing the same amount of abrasive material in a hammer mill, the badly worn steel casting (left) had a weight loss of 37 per cent while the high-chromium iron casting (right) lost only 5.5 per cent.

Fig. 2. This chrome-iron pantograph shoe had a service life of about 10 years. A tool steel that was used in similar service wore out in about 8 or 4 months; copper lasted about 24 hours.

When thoroughly backed up with zinc, the iron also has enough shock resistance to be used effectively as crushing hammers and jaw plates for many severe rock-handling jobs.

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For years, ELECTROMET high-carbon ferrochrome has been used to make chromium additions to abrasion-resistant high-chromium irons. If you should have any questions about either the production or use of these irons, write to the nearest ELECTROMET office. Our metallurgists will be glad to give many valuable suggestions and recommendations on how to make or use this iron most effectively.

Write for a free copy of the ELECTROMET publication, "Abrasion-Resistant High-Chromium Iron." This booklet is a collection of some of the best available information on how to make and to use abrasion-resistant iron castings most efficiently.

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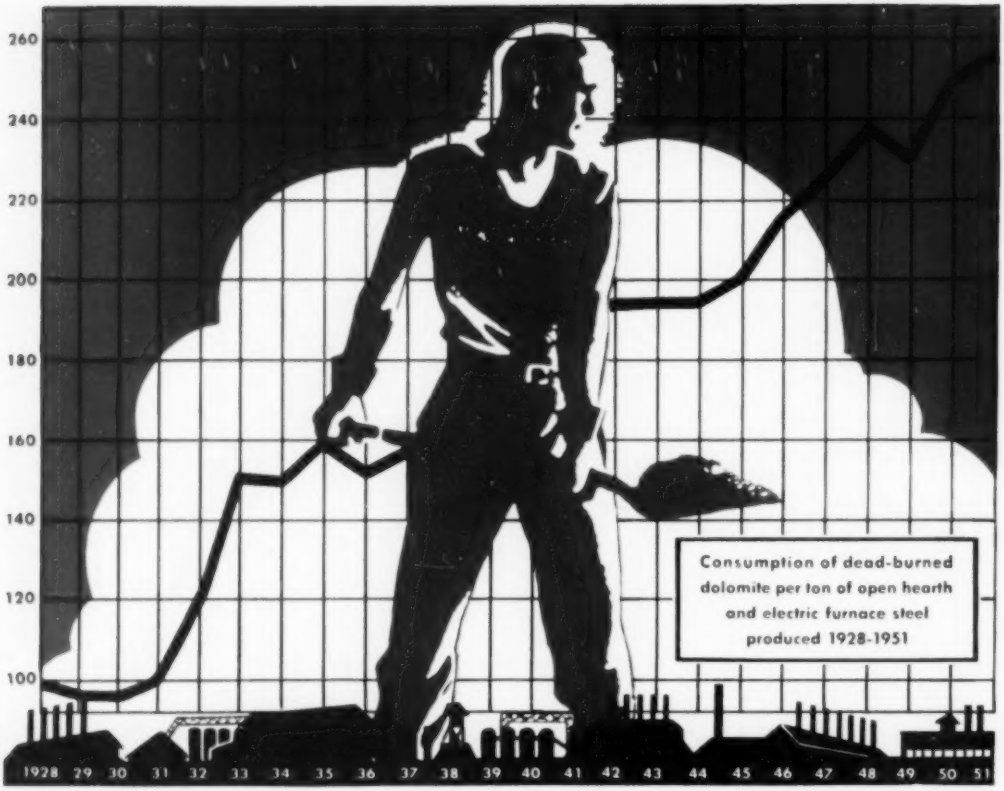

why the swing to dead-burned dolomite?

THE use of dead-burned dolomite by the steel industry has more than doubled in the past 24 years. Consumption per ton of steel is now a third higher than during the war. This steadily rising trend is due to three factors:

1. It saves time. Operation of steel furnaces at near capacity rates demands a repair material that "sets fast and stays fast". Normal maintenance with dead-burned dolomite takes no more time than is required to place the refractory.

2. It reduces bottom delays. The deteriorating quality of charge materials, fluxes and fuels contributes to increased severity of bank and bottom trouble. Proper use of dead-burned dolomite makes it possible to offset the adverse effects of these factors and keep bottom delay down.

3. It lowers refractory costs. Despite the continuing trend toward the use of more dead-burned dolomite, many shops report a reduction in total maintenance refractory expenditures, with consequently lower refractory cost per ton of steel made.

Dead-burned dolomite is now in free supply. Steel producers who have been dependent on other fettling materials can now take advantage of the economies of a dead-burned dolomite practice. Present users, too, may benefit from a more liberal use of this low-cost refractory.

With the completion of its third major dead-burned dolomite expansion in the last ten years, Basic Refractories is prepared adequately to serve the needs of the steel industry with Magnefer and Syndolag.

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1—CORE DRILL: A new drill design for drilling cored castings, through holes, and counter boring is announced by *Tilden Tool Co.* The drills are made in sizes of $^3/_4$ to 4 in. diam and up to 36 in. long. They have eight tungsten carbide cutters.

2—CLEANING COMPOUND: A free rinsing soluble liquid steam cleaning compound, safe on reactive metals and painted surfaces, has been developed by *Turco Products, Inc.* Turco 3232 is nonflammable and economically removes light to medium soil deposits.

3—COMBINATION SEPARATOR: A combination mechanical magnetic

separator especially designed to separate parts from Roto-Finish abrasive chips where both ferrous and nonferrous parts are processed is announced by the *Roto-Finish Co.* The magnetic and mechanical separating mechanisms are interchangeable on the portable frame. Model MMG 34-12 mechanical magnetic separator is driven by a 1/3 hp, 220/440, 3-phase motor.

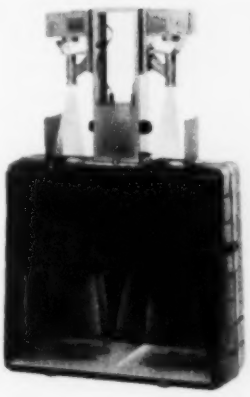
4—GAGE BLOCKS: Gage blocks manufactured from man-made metal have been developed by the *DoAll Co.* Chrome-carbide blocks have carbide hardness, but the same coefficient of expansion as steel so that it is not necessary to make corrections when checking steel parts as is necessary with tungsten-carbide blocks. Perfect stability can be expected from the new blocks.

5—LEAK DETECTOR: This instrument is designed as a tool to maintain high vacuum systems at top operating efficiency. At the highest of its four sensitivity ranges, it can detect one part of halogen in 100,000 parts of air. It also works well on very large leaks. *Distillation Products Industries.*

6—TYGON TUBING: Plastic tubing with a triple wire, stainless steel outer braid has been made available by the *U. S. Stoneware Co.* Tygon tubing absorbs vibration and does not crack, leak, or break under working pressures up to and including 300 psi.

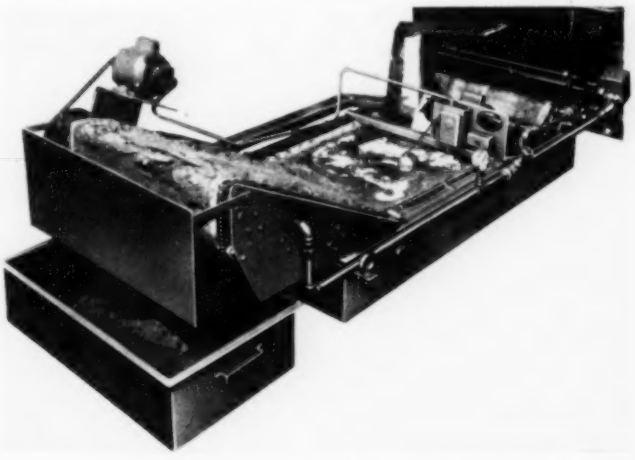
7—FLOWMETER: Accurate measurement of flow of liquids and gas under difficult conditions is made possible by the development of a new, improved flowmeter. The unit is capable of handling toxic or highly corrosive substances, viscous liquids or other fluids under pressures up to 20,000 psi and temperatures ranging from −269° to 1200°F. *Minneapolis-Honeywell Regulator Co.*

8—MORTISING ATTACHMENT: A mortising attachment of improved design has been put into production by *South Bend Lathe Works.* It consists of a fence assembly that bolts to the drill press worktable, a mortising chisel holder that clamps to the drill press quill and 3 sizes of mortising chisels and bits, $^1/_4$, $^3/_8$, and $^1/_2$ in.



10—SURFACE COMPARATOR: The faxfilm surface comparator model BL-122 has been introduced by the *Brush Development Co.* Faxfilm is the method of surface study in which a clear plastic replica of a surface is made in about a minute and projected in a microprojector to show minute details of surface condition with marked 3-dimensional effect.

9—ENDLESS BELT FILTER: Through the use of an endless belt, the Delpark Industrial endless belt filter permits the utilization of the same filtering media over and over. The Delpark filter is a continuous self cleaning gravity filter. It filters solids from liquids that will flow by gravity through filter material and discharges the solids in a relatively dry state into an outside container. *Industrial Filtration Co.*



11—BORING TOOL: Boring problems caused by the core openings which tend to deflect bar travel are eliminated with this new tool. A set of extra cutters is located between the first roughing cutters and the final finishing cutters. *Giddings & Lewis Machine Tool Co.*

12—SPRAY GUN: A spray gun with ultra sensitive controls for fine spraying has been introduced by the *DeVilbiss Co.* The spray pattern is medium sized and can be adjusted to practically pin point size for touch up work.

13—ROLLER COATERS: A new line of roller coaters is in production at the *Union Tool Corp.* The new model is equipped with three sets of rolls and automatic infeed and off bearing conveyors. Pressure on the coating rolls is applied by two 6 in. diam air cylinders that will develop 28 tones the line pressure. Pressures from 0 to 160 lb can be achieved.

Free Literature

20—COLLOIDAL GRAPHITE: Data on dag colloidal graphite dispersions used to lubricate under all conditions of extruding, forging, deep piercing, and stretch forming are contained in bulletin 426-13G. Dag dispersions protect against heat, heavy loads, and fatigue failures. Dry films of lubricant formed with these dispersions have extremely low coefficients of friction. They resist oxidation and function far above the burning point of conventional petroleum lubricants. *Acheson Colloids Co.*

21—SURFACE GRINDING: Booklet *The ABC of Surface Grinding* has been issued by the *Norton Co.* Wheels, cylinders, and segments are illustrated and described.

22—SPECIMEN MOUNT PRESS: New bulletin describing AB speed press. Features include use of preheated premolds, rapid closing and universal applications for thermosetting or thermoplastic materials in three sizes. *Buehler Ltd.*

23—METALLIC STEARATES: Revised specifications of many grades of metallic stearates are contained in booklet released by *American Cyanamid Co.* A complete list of the firm's metallic stearates for use in numerous industries is included.

24—SOLVENT DETERGENTS: Cleaning metal between processing operations, stripping paint, and cleaning action of solvent detergents are a few of the subjects covered in booklet available from *Oakite Products, Inc.* Photographs and diagrams are included.

25—MAGNETS: Catalog available from *Dings Magnetic Separator Co.* gives details on improved lifting magnet. Four point chain suspension, shock resistant all welded construction, and a finer insulating compound are a few of the improvements.

26—MOLD CASTINGS: The permanent mold foundry of the *Eaton Mfg. Co.* is described in booklet. These permanent mold gray iron castings have a dense homogeneous structure and machine to a high mirror-like finish.

27—CONVEYOR BELT: Bulletin 6915 issued by *Raybestos-Manhattan, Inc.* describes Ray-Man F, the new conveyor belt using properties of synthetic fibre strength members. It holds fasteners better, can be used where pulleys are relatively small and yet where a thick, narrow belt is used.

28—BITUMASTIC COATINGS: These protective coatings are specially formulated from a base of coal tar pitch that is, for all practical purposes, impervious to water. They stop corrosion caused by moisture, acid fumes, alkaline fumes, salt air, heat, and corrosive soil. Booklets are available from *Koppers Co., Inc.*, tar products div.

29—DESEGATIZED STEELS: Booklet entitled *Selection and Use of Desegatized High Carbon-High Chromium Die Steels* may be obtained from *Latrobe Steel Co.*

30—AUTOMATIC SOLDERING: Bulletin *Typical Results of Tocco Induction Brazing and Soldering* is now available from *Ohio Crankshaft Co.* In one particular case of switching from hand soldering to automatic Tocco soldering, solder cost was reduced 50 pct and repairs and rework due to misalignment of parts was cut 95 pct.

31—KA-WELD: Ka-Weld precast reinforced pipe insulation is explained in bulletin 2183 available from *Bloom Engineering Co., Inc.* Made of durable readily applied refractory material, Ka-Weld increases furnace output, reduces the heat loss to cooling water, reduces skid marks, slagging and sticking, and saves water.

32—STRESSPROOF: Severely cold worked, furnace treated, cold finished steel bars are used as machined. Engineering bulletin entitled *New Economies in the Use of Steel Bars* has been issued by *La Salle Steel Co.*, that gives information on Stressproof.

33—FIREBRICK: A fused mullite brick, B&W Allmul, is a unique combination of refractory properties; high hot load strength, high resistance to spalling, good volume stability, and a high melting point of 3335°F. Bulletin R-29 obtainable from *Babcock & Wilcox Co.* contains pertinent data about this firebrick.

34—STEEL SHOT: Bulletin 59-A gives information regarding Tru-Steel shot available from *American Wheelabrator & Equipment Corp.* Tru-Steel shot is made of high carbon steel that has received a full heat treatment.

35—TRANSFORMERS: Hevi-Duty specialty transformers range in sizes from ¼ to 1000 kva. The 100 kva tap changing transformer provides 36 steps of output voltage control for regulating industrial equipment. Bulletin HD-499 issued by *Hevi-Duty Electric Co.* gives detailed information.

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September

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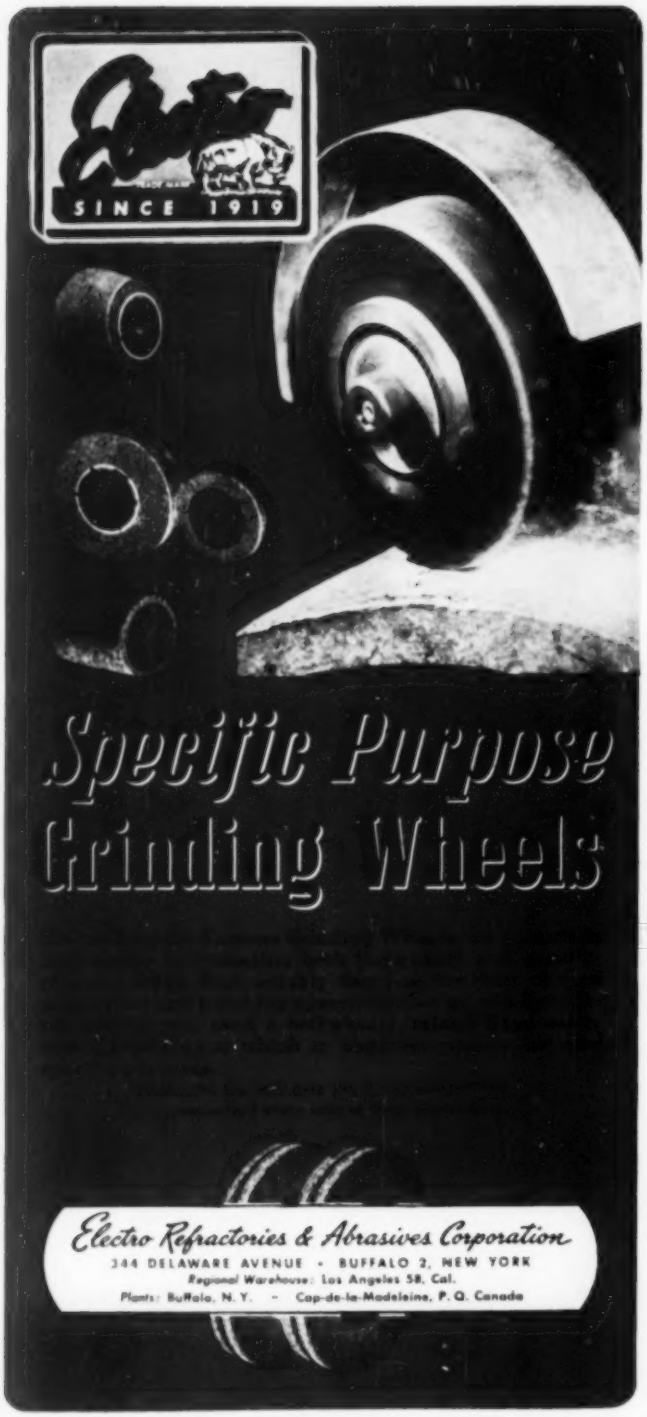
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Industrial Notes . .

• Construction on Colorado Fuel & Iron Corp.'s seamless pipe mill at Pueblo, Col., interrupted by the recent steel strike, has resumed. Completion is anticipated during the first half of 1953. The mill will have an annual capacity of approximately 150,000 tons of finished pipe and tubing when rolling an average range of sizes. Production is aimed at supplying oil and gas producers in the western and southwestern states. Cost of the mill is about $28 million.

• **Two Turkish copper plant foremen, Isfendiyar Obay and Ali Sultan Baykal, are being trained at Phelps Dodge Corp. installations under Mutual Security Agency's training program. The training of the men follows recommendations of technical assistance experts that Turkish foremen trained in the use of Gar guns, in the application of magnetite linings, and in copper casting and slag handling, would expedite the most effective operations of technical assistance modifications made under the program. Phelps Dodge was selected because the plant uses equipment identical with that being used in Turkish mines, converters of the Peirce Smith barrel type.**

• *The Lithium Compounds Industry Advisory Committee told officials of the National Production Authority that the 10 million lb expansion goal of lithium carbonate equivalents by 1955 is conservative. It has been estimated that deficits will occur between production and requirements of 1.5 million lb in 1952 and 3.5 million lb in 1953.*

• Plants are under construction by Harbison Walker Refractories, Inc. and General Refractories, Inc., in an effort to meet the demand for silica brick from the eastern Ohio-western Pennsylvania iron and steel industry. The Harbison Walker plant is going up at Windham, Ohio, near Warren at a cost of $6 million. It will have the biggest continuous tunnel kiln in the world. The General Refractories plant at North Warren will cost about $4 million. General Refractories' Los Angeles plant was recently finished at a cost of $1 million. Unburned basic brick is being manufactured on a full operation basis, increasing the company's West Coast manufacturing capacity by 100 pct.

• **Two fuel oil handling systems at U. S. Steel's Fairless works' pipe mill of the National Tube div., at Morrisville, Pa., will be constructed by the Rust Furnace Co. The**

systems will provide facilities for unloading, storage, conditioning, and recirculation of the pipe mill's fuel oil supply.

• *Aimed at speeding development work on jet engine controls, a new laboratory is being established at the Aeronautical Div. of Minneapolis-Honeywell Regulator Co. A new building will be equipped with highly complex electronic computors, controls, and relays. They will permit jet controls to be designed and proved without having to leave the ground. Jet engines will not be needed to duplicate the entire range of engine positions, idle, takeoff, cruise, speed temperature and other flight conditions.*

• Interlake Iron Ore Corp. will spend $8.5 million expanding its Chicago facilities. The largest share of the money, $6.4 million is labeled for blast furnace capacity expansion. One of the two furnaces will be boosted from a present capacity of 525 tons of pig iron daily to 850 tons. An ore receiving dock on the Calumet River has been extended 150 ft and two ore unloading bridges are being installed.

• **Negotiations have been completed with Kaiser Engineers, a div. of Henry J. Kaiser Co., for a sizeable part of the construction program at the Hanford Plutonium producing project. Kaiser is expected to start its part in the expansion during late fall 1952. Contracts for design of the new plants have been signed with Vitro Corp. of America, New York City, and the Charles T. Main Co., of Boston.**

• Vanadium Corp. of America production plans call for the output of alloys starting late in August at a new plant under construction near Cambridge, Ohio. When finished the plant will consist of a 3-section mill building containing electric arc furnaces, a research laboratory, and a pilot plant for testing and developing new products, and general offices. Initial operations at Cambridge will consist of melting secondary aluminum and manufacturing aluminum alloys. Production of ferrovanadium, low carbon ferrotitanium and other alloys is slated to begin in the spring of 1953. In the meantime, production of ferrosilicon has started in two of the five electric furnaces at the unfinished $8 million alloy producing plant at Graham, Mason County, W. Va. Two other furnaces are scheduled for early operation. The furnaces are 22 to 25 ft diam with overall rated capacity of 50,000 kw.

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Books for Engineers

Gmelin's Handbuch der Anorganischen Chemie (Gmelin's Handbook of Inorganic Chemistry), eighth edition edited by the Gmelin Institute of Inorganic Chemistry and Related Sciences in Clausthal-Zellerfeld, West Germany. System No. 41, Titan (Titanium). 827.20. 481 pp. 22 pp. index.—The Gmelin volume represents a comprehensive, critical and up-to-date review of the geology, geochemistry, metallurgy, chemistry, physics, and technology of titanium. Material is presented in such a way as to make specific topics readily available. In addition, the entire pertinent world literature, up to Jan. 1, 1950, is systematically arranged and critically reviewed. Subject matter is presented with accuracy, completeness, and conciseness.

Sauerstoff (Oxygen), System No. 3, part 2, $15.60, 218 pp.—The distribution, physical, and chemical properties, and behavior of oxygen are covered in this volume. A special section deals with oxygen isotopes. Detail treatment is given to the technology of oxygen. The occurrence, chemistry, and technology of ozone is included. One section deals with the analysis, technology of treatment, purification and distillation of water. The volume also covers the production of H.O. as well as its physical and chemical properties.

Arsen (Arsenic) System No. 17, $33.33, 475 pp.—A comprehensive review is made of the geology, geochemistry, chemistry, physics, and technology of As and As compounds. Information on technical application is included. Particular accent is placed on insecticides, and in the glass, concrete, and rubber industries. Of particular interest is the treatment of arsenic hydrogen compounds and/or arsenic acids, their solutions, and their chemical reactions.

Magnesium, System No. 27, part A4, $24.00, 356 pp.—This part completes the Gmelin Mg volume. It covers binary and ternary alloys from Mg-Zn to Mg-Re, as well as surface treatment of Mg and Mg alloys. Thirty one binary and 105 Mg alloy systems of higher order are treated for which the following material is given: Phase diagrams, data on intermetallic compounds, production processes, casting methods, structural data, hardening characteristics as well as crystallographic, thermic, optical electric, magnetic, and electrochemical properties. Chemical behavior and corrosion resistance are treated in detail.

Management Controls in Industrial Research Organizations, by Robert Anthony assisted by John S. Day. *Harvard University*. $6.75, 537 pp., 1952.—The book is written primarily for those in management positions in industrial research organizations. While business organizations have developed useful control techniques for production, finance, marketing, and other areas, progress for the research function has not been as rapid. The book recognizes the difference between research and the rest of the firm. The author concludes that the problem involved is the maintaining of proper balance between "freedom at the laboratory level and direction from the top."

Welfare Services In the Iron and Steel Industry; Vocational Training and Promotion in the Iron and Steel Industry, and General Report of the Iron and Steel Committee of the International Labor Organization. *International Labor Office*, $1.50 per set of three, 1952.—The books cover the reports made by the Iron and Steel Committee of the International Labor Organization. The volume on welfare presents points of similarity and difference between some of the more important welfare provisions made by the industry in various countries. Vocational training is treated in an overall manner concerning the situation in few countries and supplies data for a basis of comparison on aims and technical qualifications demanded in the production trades.

Metallurgy for Engineers, by John Wulff, Howard F. Taylor, and Amos J. Shaler. *John Wiley & Sons*. $6.75, 624 pp., 1952.—The book is based on material used by the authors for five years in teaching a course at the Massachusetts Institute of Technology. The text is not intended as a source of data for the practicing engineer. Rather, it is to be used to refresh in his mind the concepts of metallurgical engineering which he may have forgotten, or was not taught at school. The first part of the book is concerned with principles and the last part with processing practice.

Practical Metallurgy for Engineers, fifth edition, *a publication of the research staff of E. F. Houghton & Co.* $3.50, 599 pp., 1952.—The fifth edition of this book represents the latest standards and practices followed by the metal industry and includes a discussion on future probabilities relating to new materials, new alloying elements, and new types of heat treatment. New chapters include one on flame and induction heating, bringing in new developments which

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Correction

The Academic Press, Inc., publishers of Diffusion in Solids, Liquids, Gases, was incorrectly listed as the Academic Free Press, Inc., in the June issue of JOURNAL OF METALS.

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have expanded the useful range of both methods. The chapter on heat treatment of aluminum alloys has been expanded to heat treatment of nonferrous alloys.

Corrosion Testing Procedures, by F. A. Champion. *John Wiley & Sons*, $6.25, 369 pp., 1952—In view of the wide variety in the objects of corrosion tests, the book is divided into stages. Alternative procedures in each stage are described separately. The stages include: The choice and preparation of metal and corrosive; exposure of the metal to the environment in laboratory, field or service tests; cleaning of the specimens preparatory to examination; examination of the specimens or the corrosive for the effects of corrosion (other measurements which indicate the tendency to corrode rather than the effects of corrosion, and special tests, are considered separately); and the expression and interpretation of results, with particular reference to the form of the corrosion or time curve.

Geology, by O. D. von Engeln and Kenneth E. Caster. *McGraw-Hill Book Co., Inc.*, $7.00, 730 pp., 1952—The book is aimed at supplementing the work of the instructor without being encyclopedic. The treatment is always sound and logical as it attempts to relate geology to the broader field of life. The facts of historical geology are presented as an outgrowth of the understanding of physical geology—in keeping with the fundamental law of geology that "present agencies and forces, acting through enormous time, have shaped the world as we see it—the law of uniformitarianism."

Fractional HP Electric Motors, by F. G. Spreadbury. *Sir Isaac Pitman & Sons, Ltd.* 35s, 342 pp.—Detailed treatment of the more important types of these small motors is given, beginning with two chapters on dc units. Polyphase and singlephase induction motors are discussed in subsequent chapters, along with the universal, repulsion, and synchronous motors. Brief consideration is given to hysteresis, permanent magnet, and other miscellaneous types of motors. Separate chapters are devoted to motor control and to performance characteristics.

Michigan Copper and Boston Dollars, by William B. Gates, Jr. *Harvard University Press*, $5.00, 301 pp.—Apparently based on extensive research, the book deals with one of the copper mining regions of the U. S. It covers the following periods: 1845 to 1866, opening of the Michigan lodes; 1867 to 1884, period when Michigan copper dominated the domestic market; 1885 to 1904, period of struggle for domestic and world leadership; 1905 to 1918, mature period of the industry; 1919 to 1938, the decline of Michigan copper mining, and World War II and the future.

Handbook of Engineering Fundamentals, second edition, edited by Ovid W. Eshbach. John Wiley & Sons, $10.00, 1952—The book is a companion volume to the Wiley engineering handbook series, and contains the fundamental laws, theories and data basic to engineering practice. Sixteen years of experience have dictated changes, deletions, and additions to the first edition. Greater emphasis has been placed on the MKS system of units. Subject matter is essentially an extended summary of the principles of mathematics, physics and chemistry, commonly used mathematical tables, properties and uses of materials, and the mechanics of solids and fluids. Also included is a discussion of engineering law.

Carbide Cutting Tools, by Warren Baker and Joseph S. Kozacka. American Technical Society, $5.50, 416 pp., 1952—The authors have included a great deal of previously unpublished material. The book provides a comprehensive treatment of the design, manufacture, use, and maintenance of cutting tools using carbide as the cutting edge. General aspects are dealt with first, followed by chapters on particular tool types, speeds and feeds, selection of carbides and other subjects.

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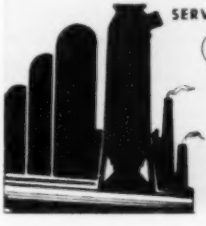

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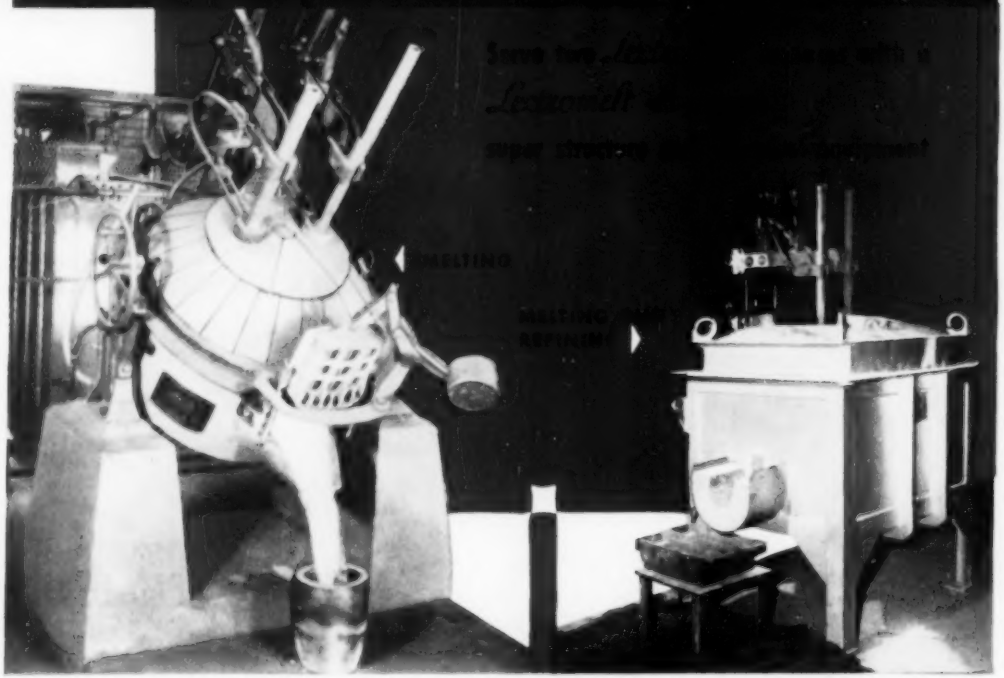

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Coming Events

July 1-Sept. 30. Centennial of Engineering, Chicago.

Sept. 3-6. AIME, fall meeting, Palmer House, Chicago.

Sept. 3-6. AIME, Industrial Minerals Div., annual fall regional meeting, Chicago.

Sept. 3-15. AIME, Chicago Section, Centennial of Engineering, Chicago.

Sept. 4-5. National Conference on Industrial Hydraulics, Hotel Sherman, Chicago.

Sept. 5. AIME, Iron & Steel Div., Centennial of Engineering, Chicago.

Sept. 5-6. Engineers' Council for Professional Development, annual meeting, Hotel Sherman, Chicago.

Sept. 9. Society for Applied Spectroscopy, informal dinner, Tosca's; business meeting, Socony Vacuum Training Center, New York.

Sept. 10-12. Porcelain Enamel Institute, annual shop practice forum, University of Illinois, Palmer House, Chicago.

Sept. 11-13. American Institute of Chemical Engineers, Palmer House, Chicago.

Sept. 18. AIME, Utah Section, Newhouse Hotel, Salt Lake City.

Sept. 22-23. Canadian Institute of Mining and Metallurgy, annual geological excursion, New Sherbrooke Hotel, Sherbrooke, Que.

Sept. 22-25. American Mining Congress, Metal and Nonmetallic Mining Convention and Exposition, public auditorium, Denver.

Sept. 23-25. Institution of Mining and Metallurgy, symposium on mineral dressing, Royal School of Mines, London.

Sept. 30. AIME, Morenci Sub-section, Longfellow Inn, Morenci, Ariz.

Sept. 30-Oct. 3. Assn. of Iron and Steel Engineers, exposition and convention, Cleveland Public Auditorium, Cleveland.

Oct. 1-3. National Assn. of Corrosion Engineers, South Central Region, Jung Hotel, New Orleans.

Oct. 3. AIME, Southern Ohio Section, National Open Hearth Steel Committee, Desher-Wallick Hotel, Columbus, Ohio.

Oct. 10. AIME, Eastern Section, National Open Hearth Steel Committee, Warwick Hotel, Philadelphia.

Oct. 10. AIME, Southwestern Section, National Open Hearth Steel Committee, Peoria, Ill.

Oct. 15-17. Canadian Institute of Mining and Metallurgy, annual western meeting, Royal Alexandra Hotel, Winnipeg.

Oct. 20-21. Special Libraries Assn., metals section, regional meeting, National Metal Congress, Philadelphia.

Oct. 20-22. AIME, Institute of Metals Div. fall meeting with National Metal Congress, Hotel Adelphia, Philadelphia.

Oct. 20-24. National Metal Exposition and Congress, Philadelphia.

Oct. 20-24. American Welding Society, meeting with National Metal Congress, Bellevue-Stratford Hotel, Philadelphia.

Oct. 20-24. American Society for Metals, meeting with National Metal Congress, Benjamin Franklin Hotel, Philadelphia.

Oct. 20-24. National Safety Congress and Exposition, Conrad Hilton, Congress, Morrison, LaSalle, and Sheraton Hotels, Chicago.

Oct. 22-23. Society for Nondestructive Testing, meeting with National Metal Congress, Hotel Sylvania, Philadelphia.

Oct. 30-31. AIME, Fuels Conference: Coal Div., AIME; Fuels Div., ASME, Bellevue-Stratford, Philadelphia.

Nov. 4. AIME, Morenci Sub-section, Longfellow Inn, Morenci, Ariz.

Nov. 7. AIME, Pittsburgh Section, National Open Hearth Steel Committee, off-the-record meeting, Hotel William Penn, Pittsburgh.

Nov. 18. AIME, Buffalo Section, National Open Hearth Steel Committee, Hotel Statler, Buffalo.

Nov. 20-21. American Society for Quality Control, Midwest Conference, Claypool Hotel, Indianapolis, Ind.

Dec. 4-6. AIME, Electric Furnace Steel Conference, Hotel William Penn, Pittsburgh.

Dec. 7-10. American Institute of Chemical Engineers, annual meeting, Hotels Cleveland and Carter, Cleveland.

Dec. 8. AIME, Arizona Section, all day meeting, Tucson.

Jan. 26-30, 1953. American Society of Heating and Ventilating Engineers, international heating and ventilation exposition, International Amphitheatre, Chicago.

Feb. 16-19. AIME, annual meeting, Statler Hotel, Los Angeles.

Mar. 16-20. National Assn. of Corrosion Engineers, annual conference and exhibition, Hotel Sherman, Chicago.

Mar. 23-27. ASM, western metal congress and exposition, Pan-Pacific Auditorium, Los Angeles.

Apr. 12-May 23. Empire Mining and Metallurgical Congress, Australia-New Zealand.

Apr. 20-22. AIME, National Open Hearth and Blast Furnace, Coke Oven and Raw Materials Conference, Hotel Statler, Buffalo.

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METALLURGY for ENGINEERS

Casting, Welding and Working

By John Wulff, Howard F. Taylor, and Amos J. Shaler, *The Massachusetts Institute of Technology*

THIS thorough volume explains the concepts and principles that underlie metal processing from ingots to finished articles of commerce, and the processes themselves. *Metallurgy For Engineers* is of value both to engineers and metallurgists. Each chapter concludes with a summary and list of definitions, reviewing the material contained. Particular emphasis is placed on the solidification of metals and the fundamentals of both physical metallurgy and metal processing.

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Journal of Metals

AN important part of Pier 57 floated down the Hudson River recently, but it was planned that way. The first section of the New York City addition to waterfront facilities was constructed at Haverstraw, N. Y., and then transported via the Hudson. One innovation in the concrete, box-like superstructure was the prestressed concrete stringers that support the main deck of the pier.

The prestressing beds are near the clay pit in which the three concrete-box superstructures of the pier are being fabricated. The beds are 350 ft long and 12 ft wide. Mass production is achieved by stressing steel reinforcing wires the full length of the bed, then casting concrete around them in 16 sections, each 19 ft long. Three full-length castings are made at one time. The prestressing beds are turning out 48 stringers daily.

The American Steel & Wire div. of U. S. Steel has been manufacturing high tensile steel wire for about 15 years, mainly for use in the manufacture of prestressed concrete pipe. Metallurgical research was undertaken to provide a wire that would stand up to the specification of structural applications.

The result was the high carbon steel rods produced at the Worcester, Mass. plant of American Steel & Wire and shipped to the company's plant at Trenton, N. J. At Trenton they are cold drawn to 0.192 in. diam and then stress relieved by special heat treatment.

The finished wire has an ultimate strength of more than 240,000 psi. In the 350-ft prestressing beds the wires are locked at each end in groups of 10 each into Freyssinet cones. Two hydraulic jacks exerting a 224 ton pull, stretch the wires to an initial stress of 160,000 psi or 67 pct of their ultimate strength. This is done with an elongation in the wire of 24 in.

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WHAT does John L. Lewis want this time? No one seems to know. The only certainty is that he has given notice of termination of the present contract between the United Mine Workers and coal mine operators, effective September 20. A lot of people are wondering, however, if Lewis has not chosen the wrong time to renegotiate. The bituminous coal industry is in one of its worst slumps in history. Many mines closed down because of the steel strike and stockpiles are abnormally high. The usual tradition of the UMW is "no contract no work," but it remains to be seen whether the slogan will be an effective weapon this time.

However, one thing must be taken into consideration. John Lewis is a man who knows the economics of his industry. He knows that coal mining is in one of its most critical periods. Soft coal markets have been extremely weak, and coal stocks above ground are between 70 and 80 million tons. Lewis must be aware that under these conditions, his bargaining position is not particularly strong.

Predominantly, it is felt that the UMW will make some straight wage demands, and possibly attempt a shortening of the work day from 8 to 7 hr. The union may also ask for an increase in the welfare levy of 30¢ per ton mined. Lewis may not attempt to force through a full schedule of demands, if for no other reason that public opinion may not see fit to side with him. A prolonged coal strike, following the steel shutdown, could find itself in the midst of an unsympathetic public. Thus, many observers look for Lewis to ask for less than he usually does.

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BRAZIL will probably remain unchallenged as the largest steel producer in Latin America. Expansion programs and new steelmaking companies will keep the country well ahead. Brazil produced some 900,000 tons of steel ingots in 1951, far more than the 390,000 tons produced in Mexico. Chile, the only other South American country with fully integrated steel plants, ranked third with a production of 200,000 tons. Largest Brazilian steel producer is Cia. Siderurgica Nacional at Volta Redonda, producing over 300,000 tons of steel per year. Expansion plans underway are expected to boost production to 600,000 tons. Products consist mainly of rails, sheet, and heavy rolled structural shapes. Rated as second largest is Cia. Belgo-Mineira, with a capacity of 200,000 tons per year. Small rolled shapes dominate output.

A newcomer is Cia. Aceo Especiars Itabira, known as Acesita. Acesita is located near a good source of hydroelectric power, and is close to the railroad line

The Flex Tester was developed and is being used by Jones & Laughlin Steel Corp. for measuring resistance to bending as a means of determining the drawing quality of cold reduced sheet and strip steel.
Using the Flex Tester, the operator bends back a corner of the steel sheet, and the resistance to the bend is measured on a dial on the Flex Tester. Numerous tests have indicated that 60 on the gage is an approximate dividing line between steel that can be drawn and steel that might not take the draw. After the Flex Tester reading, a spherometer measures the diameter of the bend. The smaller the diameter, the greater the tendency to stretcher strain. If the spherometer shows a large diameter bend, about 3 in. or more, there will be no tendency to stretcher strain. C. B. Buker, of J & L, inventor of the Flex Tester, demonstrates the spherometer part of the operation. The sheet has just passed through a roller leveling machine. J. R. Speer of J & L's technical dept. collaborated on the development of the Flex Tester.

from Itabira to Victoria. The iron ore properties at Itabira, the railroad, and port facilities at Victoria belong to Cia. Vole do Rio Doce. Acesita has installed what is considered to be the largest charcoal burning blast furnace in operation, with a capacity of 200 tons per day. Steel is produced by the duplex process, utilizing a Bessemer converter and a 20 ton electric furnace. Products consist of specialty items not generally made in Brazil, such as forgings, low and high carbon rolled sheet, spring steels, high silicon sheet, and special alloys.

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THE steel strike is over, and the United Steel Workers, lead by Phil Murray, gained almost all of their original objectives. But the repercussions of the 58-day strike will be felt by the union, management, and the public for many months. Perhaps the people who will take the worst beating are the steel consumers, who will feel the pinch, according to some authorities, well into 1953. By August 2, over 17 million tons of steel were lost to the nation. Even with steel plants swinging into high gear quickly, the loss cannot be made up.

The steel settlement brought a wave of wage increases in other related branches of the metals and mining industry, and others can be looked for in the future. Whether the additional wages will be of benefit to the workers is doubtful. The Office of Price Stabilization has already announced that Mr. Citizen can expect the cost of living to rise about $100 per year based solely on steel prices. Steel won its increase per ton and labor made superficial gains, but in the final analysis the nation is apt to find itself in a worse fiscal and economic situation than ever, with the added burden of a lagging national defense. The Army announced that ammunition must be rationed, with top priority going to the Korean front. Use of live ammunition in training is being curtailed, and National Guard units will get drastically reduced supplies. Thus, many men will go into combat without adequate training. Experts are now wondering who won what.

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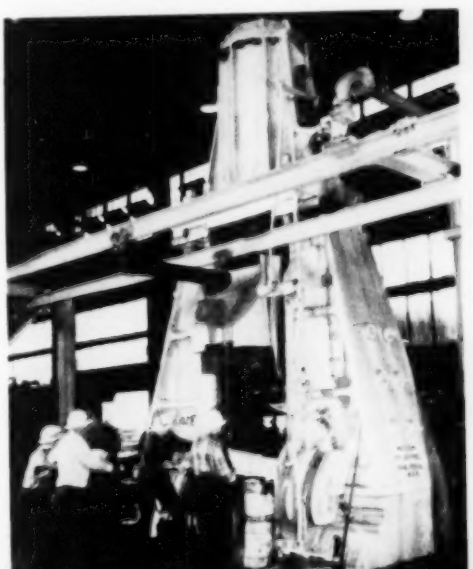
THIS can be one of the most momentous autumns in the history of Great Britain. The Conservative party is expected to introduce legislation for the denationalization of the steel industry. Thus, they take to the field to challenge the most sacred of sacred cows of the Labor party. The Conservatives came into office on the promise that they would return steel to private ownership. The Laborites are certain to use every weapon at their command to fight denationalization and the current Government is aware that it will be a battle to the finish. They are also aware that it may drag on for several years and through several governments. They tacitly admit that the field may not be won for some time, with the statement that it "may take some years" before the industry is restored. The statement appears to gainsay that the Conservatives recognize the strong possibility of a return of the Labor government at the next election and any action by Parliament now could be easily undone. It is quite possible that the steel issue itself will force another election. If so, the British people again will have to make the choice. They voted for denationalization the last time, but since then, the economic situation, both domestically and in connection with Britain's foreign trade, has grown steadily worse. It may be that indirect issues will serve as the vehicle for the continuation of a nationalized steel industry.

The two approaches that the Conservative Government intends to take will by no means remove the Government from the steel industry.

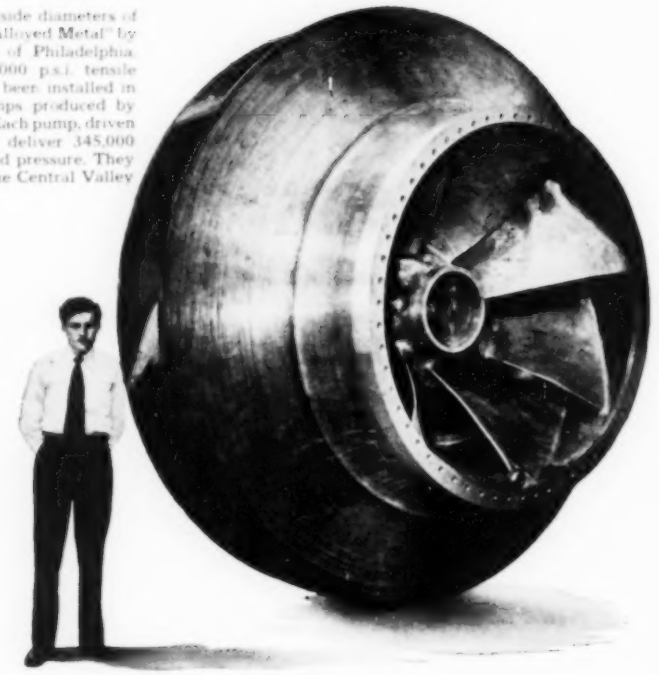
One part of the bill to be presented to Parliament, if passed, will create an iron and steel board to supervise the industry as a whole, ending the distinction between major units that were nationalized and minor plants still in private hands.

Secondly, the Government-owned Iron & Steel Corp. will be dissolved. The corporation holds the securities of the nationalized steel mills. In its place, a holding and realization agency will be created to dispose of those securities to private owners. Considering the uncertainty of government, it is debatable that private risk capital will be forthcoming. The former management of the plants may be content to sit back for some time to await political developments. Until denationalization attains a solid footing, it may appear foolhardy to investors to put money back into steel without assurance that they will be allowed to operate the mills privately.



The new 40,000 lb drop forge hammer at Kropp Forge Co. works, Chicago is kept busy turning out parts for the ever growing U. S. Air Force. The hammer is part of a $4.5 million improvement and expansion program at Kropp, and is one of the largest of its kind. It weighs almost 1 million lb, with a concrete and steel foundation extending 40 ft below the floor's surface.

Six giant impellers like this one, with outside diameters of 145", were produced in "Turbine Nickel-Alloyed Metal" by American Manganese Bronze Company of Philadelphia. Meeting minimum specifications of 80,000 p.s.i. tensile strength, and 20% elongation, they have been installed in 84" vertical volute, bottom suction pumps produced by Worthington Corporation, Harrison, N. J. Each pump, driven by a 22,500 H.P. motor, is designed to deliver 345,000 gallons per minute against a 197-foot head pressure. They provide water for irrigation purposes in the Central Valley Project, in California.



How a little Nickel Buys a lot of Endurance

. . . is shown by six 24-ton Impellers Cast in Nickel-Alloyed Manganese Bronze

This large casting is one of six identical 48,000-pound impellers cast in "Turbine Nickel-Alloyed Metal" . . . a manganese bronze containing 2 to 4 per cent nickel.

The nickel addition increases not only its strength but also its resistance to both erosion and corrosion. Nickel provides a tenacious surface film that retards corrosion penetration and dezincification.

Experience shows that small amounts of nickel in standard bronzes increase yield strength and shock resistance as much as 25 to 50%. In addition to being a grain refiner and alloy diffuser, nickel increases fluidity of the molten metal, thus helping to minimize misruns and to improve density and pressure-tightness.

At the present time, the bulk of the nickel produced is being diverted to defense. Through application to the appropriate authorities, nickel is obtainable for the production of nickel bronzes for many end uses in defense and defense supporting industries.

INCO

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American capital may finance construction of two steel producing plants, one in the West Indies and another near Mazatlan, on the west coast of Mexico. Both plants will be based on local ores. Electric reduction may be employed at the Mexican plant because of lower cost.

The Defense Production Administration has set a goal of 2½ million long tons of manganese ore by 1954, an increase of 630,000 tons per year over the 1950 total of 1.87 million tons. DMPA also wants 1.3 million tons capacity for the production of galvanized sheet and strip steel by 1954. Columbite and tantalite ore goals for the same year were set at 3 million lb.

Defense Materials Procurement Agency and E. I. duPont deNemours & Co., have reached an agreement calling for the tripling of the company's output of titanium over the next five years. Producing facilities at Newport and Edge Moor, Del., will be expanded, aided by a Government advance of $14.7 million.

Two new methods for the economic manufacture of thin tantalum foil used in small electrolytic capacitors, the rolling and vapor disposition approaches, are described in PB 105600, final Report on Investigation of Manufacture of Electrolytic Capacitors for Low Temperature Operation. The report may be obtained from the Library of Congress, Photoduplication Service, Publication Board Project, Washington, D. C.

Cadmium consumption in the U. S. declined from 9.54 million lb in 1950 to 7.17 million lb in 1951, because of restrictions on end use placed by the National Production Authority. Primary production declined 10 pct in 1951.

Tellurium copper alloy, with machinability nearing that of free-cutting brass and electrical conductivity 90 pct of pure copper, is available from Chase Brass & Copper Co., Waterbury, Conn. The alloy is especially adaptable to mass production of electrical and electronic connectors. Use of the alloy is advantageous in comparison with leaded copper or leaded high copper alloys because hot working properties of copper are greatly reduced when small amounts of lead are added.

The biggest blast furnace in Britain has gone into operation at Margam, Wales, alongside of the Margam steel plant, which is partly equipped with American machinery. The furnace hearth is 25 ft 9 in. diam and can turn out 1000 tons of iron daily.

U. S. aluminum production for the first half of 1952 was 17 pct greater than a similar period in 1943, with a total of 923,072,606 lb produced. It was 14 pct more than turned out during the first six months of 1951 and 13 pct more than the industry produced during all of 1946.

Kaiser Aluminum & Chemical Corp. awarded the contract for construction of new aluminum forging facilities at Newark, Ohio to Darin & Armstrong. The contract, in connection with the Air Force heavy press program, calls for construction of the principal heavy press plant and auxiliary buildings.

THE DRIFT OF THINGS

by Edward H. Robie

New Name for the Institute?

SHOULD the name of our Institute be changed? Perhaps one should say, should it again be changed, for until 1919 the name was the American Institute of Mining Engineers. When the American Institute of Metals joined our ranks we became the American Institute of Mining and Metallurgical Engineers. To make it a full mouthful, and strictly legal, one should add the word "Incorporated."

At the June meeting of the Board of Directors it was suggested that this name was not a particularly happy one, especially so far as members of the Petroleum Branch, comprising a quarter of our membership, were concerned—not particularly appropriate as the name for the professional society for petroleum engineers. Apart from the petroleum group, the present name is felt by some not to be sufficiently comprehensive. Most geologists and many metallurgists, ceramists, and fuel technologists, for instance, are not engineers. They could never qualify as registered professional engineers under the licensing laws and yet they are valued and fully qualified Members of the AIME.

The Directors, at the June meeting, thought the idea of a change in name should be presented to the membership for discussion, and suggested this column as the avenue of approach.

Nine years ago Dean Steidle, of Penn State, recommended among other things that the name of the Institute be changed to "American Institute of Mineral Technologists and Engineers." In an editorial in *Mining and Metallurgy* in January 1944 objection was offered to this name but "American Institute of Mineral Engineers" was suggested. A special committee appointed by the Board to review Dean Steidle's suggestions (W. B. Heroy was Chairman) suggested that if the AIME were starting from scratch, the American Institute of Mineral Engineers might be a preferred name. It was not thought that the change suggested by Dean Steidle was one of major importance, and the comment was made that "the present name has gained prestige through many years and is cherished by our membership. An important element of 'good will' is attached to it and some of this would be unquestionably sacrificed by any change."

In *M&M* for February 1945, Oliver C. Ralston went into the derivation of the terms mineralogy and metallurgy, and pointed out that both Mining and Metallurgical mean "digging," etymologically. He went on to show, with tongue in cheek, that if we want a short and all-inclusive name it should be American Institute of Geo-urgists, or, for euphony, Geolurgists. Oliver's brilliant development seems to have been received with speechless wonder!

Should a decision ever be made to change the name, we think most members will agree that the American Institute of Mineral Engineers is to be preferred over anything yet suggested. "Mineral" has become through usage a much broader term than is indicated in the dictionary. Webster states that a mineral, in the true sense, must be inorganic, but Murray's Oxford English Dictionary seems more liberal, defining "mineral" as "any substance which is obtained by mining; a product of the bowels of the earth," and "mineral oil" as any oil of mineral origin, as petroleum or shale oil. Certainly "the mineral industry" is ordinarily taken to include those activities based upon processing all the metallic and nonmetallic ores and deposits found in the ground, including the fuels. One advantage of this title is that the familiar abbreviation, "AIME," need not be changed. The advisability of maintaining a well-known abbreviation is evident, and was recognized, for instance, when the Committee for Industrial Organization became the Congress of Industrial Organizations some years ago.

But if the petroleum engineers are the ones to be chiefly considered in revising the name of the Institute, it is by no means certain that they would feel that they are much more adequately recognized in a group of Mineral Engineers than in a society of Mining and Metallurgical Engineers. And then there remain, of course, the considerable number of professional members of the Institute who are not engineers at all.

Comment from readers is invited.

Labors of Love

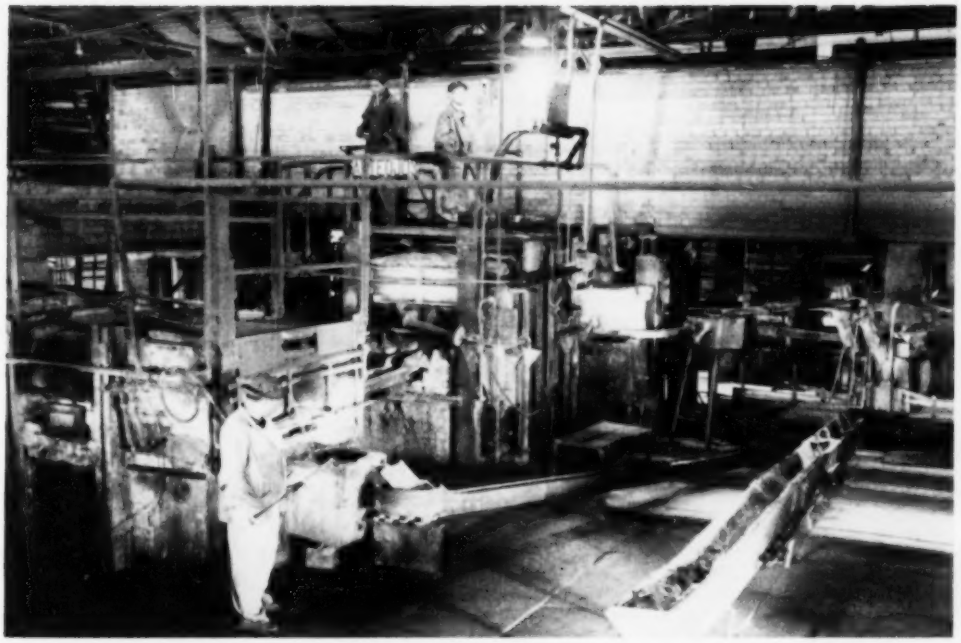
Few members of the Institute ever stop to think of the time, thought, and money that is given freely and generously by hundreds of members to their professional society. A large part of the President's year is devoted to traveling about the country for the society, to attending meetings, and to reviewing matters on which his counsel is needed. Most of the Directors, particularly those who are able to come to frequent meetings, also take their jobs seriously. Branch, Division, and Local Section officers, particularly Chairmen and Secretaries, find that many hours a month are required, which usually means that much less leisure time at home. Several hundred members serve on Institute committees, which may require scarcely any time or may require a day's work a month. Such committees as the Admissions Committee and the various Technical Publications committees are among the more active and hard-working groups. Many who are not on any committee still find they are called on for work. Such, for instance are those especially skilled in specific fields who are asked to review critically technical papers submitted for the Transactions.

It is true that most of those who thus contributed to the work of the Institute benefit themselves by so doing, by widening their knowledge and their circle of friends and acquaintances in the profession, but for most this is a byproduct of their work and not the reason for their acceptance of such professional responsibility. Many of our workers are at or near the top in their companies so added recognition from Institute work means little to them.

Undoubtedly no living member of the Institute has given more of his time to its affairs, or has been a more diligent, able, and devoted guardian of its material well-being, and supporter of its traditional purposes and tenets, than Erle V. Daveler, who retired from the Board last February after 23 full years of service as a Director. For nine years he was Vice-President. He served as Chairman of both the Executive and Finance Committees of the Institute, and is still Chairman of its Committee on Investments. Before coming to New York he served on professional committees and contributed to the Transactions.

Such men as Erle Daveler, and conspicuously he, have brought the AIME to its present stature.

At the suggestion of the Board, President Haider recently transmitted to him a letter of appreciation. In replying he said, "I have always considered it a deep privilege to serve the Institute, and through my association with it there have resulted friendships with the finest group of men I know of in any organization, who all unselfishly have served it."



The continuous softening and desilverizing process completely replaced the old batch softening methods and the Parkes process at the Monterrey lead refinery. In the softening furnace shown, the softener unit is at right, and slag treatment at left.

Monterrey Refinery Uses Continuous Lead Softening And Desilverizing Process

by G. Ross and S. A. Peabody

THE lead refinery of the Compania Metalurgica Penoles, S. A., at Monterrey, Nuevo Leon, Mexico, is the first on the American continent to use the continuous softening and desilverizing process developed by the Broken Hill Associated Smelters, Pty., Ltd., of Port Pirie, South Australia.

In comparison with the Parkes process, the operation requires less labor, but is more costly in repairs and maintenance. Desilverization is easier and more complete, and zinc consumption is slightly lower. Tonnage is more flexible with a fixed crew of men.

Bullion is received by rail in $3\frac{1}{2}$ ton blocks from the company smelter in Torreon, Coahuila. A small amount of custom bullion from various minor smelters is also treated. Currently the refinery is treating up to 7000 tons of bullion a month containing as impurities about 0.02 pct copper, 1 pct antimony, 0.5 pct arsenic and 0.1 pct bismuth, together with about 1 oz of gold and 100 oz of silver per ton.

G. ROSS and S. A. PEABODY are associated with Cia. Metalurgica Penoles, S. A., Monterrey, N. L., Mexico.

Decopperizing

The bullion is melted in 140-ton kettles for sampling and decopperizing. The copper is reduced to less than 0.01 pct by counter-current drossing with sulphur. After drossing, it is passed to another kettle for sampling and then held in a storage kettle from which it is fed to the softener unit.

The dry drosses from decopperizing operations are sampled and then smelted in a reverberatory furnace to produce speiss and matte for shipment to a copper smelter, and lead which is returned to the premelter kettles.

Continuous Softening and Desilverizing Process

Experiments in continuous softening were carried out with a small experimental furnace installed in 1936. Sufficiently good results were obtained to indicate further pilot plant tests, but for various reasons no further work was done until 1943. At that

Desilverized lead pours continuously from the desilverizing kettle into the surge kettle. The remaining zinc-silver-lead alloy is dipped and molded for retorting when the silver builds up to about 20 pct

time, another experimental unit was installed which gave good results and was finally incorporated into the plant flowsheet. With the construction of a second unit in 1946, the old batch softening process was discontinued.

In 1947, planning began for the installation of a continuous desilverizing unit. The problem was complicated by the limited headroom and the lack of floor space available in the existing plant, as well as the necessity of continuing operations by the Parkes process until the new continuous process could be placed in satisfactory operation. The new unit was ready for trial in July 1949. The usual troubles of starting a new process were encountered, chiefly because of a lack of trained personnel. In a short time, however, good results were obtained and the process is now operating smoothly. The Parkes process has not been used for desilverizing since 1949.

The softener unit is a brick lined, water jacketed reverberatory furnace heated by natural gas. Interior dimensions of the furnace are 4x10x3 ft at the break of the arch.

Lead to be softened is pumped continuously from a small surge kettle and enters the side of the furnace through a submerged inlet. The lead bath is maintained at a depth of 18 in. Air at 40 to 50 psi pressure is introduced in the hot bath by means of replaceable ¾ in. steel pipes entering through the top of the furnace to agitate the lead bath. The oxidation reactions set up by the violent agitation normally produce enough heat during operation to maintain its reaction temperature without use of gas. Softened lead containing 0.001 pct or less of arsenic and about 0.05 pct antimony is discharged continuously from a submerged outlet at one end of the furnace. Slag formed of the oxides of lead, arsenic, and antimony is tapped periodically from the opposite end of the furnace and discharges to a small reverberatory furnace where it is rabbled with coal to produce a high antimony slag and a hard lead which is returned to the softener. The antimonial slag is smelted in a cupola furnace to produce antimonial lead of various grades.

The softened lead from the continuous softener is carried in open launders to a temperature control furnace in which it is heated to 650 C. From this furnace the lead is fed continuously to one of the duplicate desilverizing units.

The continuous desilverizing kettle is the shape of an elongated egg set up on one end and divided horizontally into four cast iron sections, with a total depth of 18 ft and maximum diameter of 8 ft. The kettle is incased in a brick furnace or housing divided into four separate hearths, corresponding to the four sections of the kettle. Each of these hearths can be heated independently by gas burners, or cooled by drawing air through the hearth. Once in operation, the kettle is always full of bullion. A layer of molten zinc is established in the top part of the kettle, over the lead, to a depth of about 40 in.

The incoming lead enters at the top of the kettle, passing downward through the zinc or the zinc-silver-lead alloy which forms in the top part of the kettle, and which is maintained at a temperature of 590 C by continuous firing. It flows slowly downward to the bottom of the kettle reaching a temperature of about 322 C at the bottom.

In passing through the zinc alloy, the lead becomes saturated with zinc at this high temperature, leaving most of the gold and silver alloyed with the zinc. As it enters the second section, it is subjected to strong cooling and becomes supersaturated with dissolved zinc-silver-lead alloy that separates and rises to the top. Moderate cooling by radiation is continued in the lower sections. As the temperature drops lower, the zinc-silver-lead alloy continues to separate and rises to the alloy layer at the top. Thus a continuous lead impoverishment, alloy enrichment cycle is set up. Desilverized lead is withdrawn continuously from the bottom of the kettle up through the siphon pipe and discharged to the surge kettle. The zinc-silver-lead alloy is allowed to enrich to about 20 pct silver, and is then dipped and molded in blocks of convenient size for retorting. After dipping, the alloy bath is rebuilt immediately with fresh zinc and the enrichment cycle begins again.

The temperature gradient over the entire height of the kettle is obtained by means of the four separate hearths, corresponding to the four sections of the kettle, which are connected to an exhaust fan to give constant forced draft. The main cooling is applied to the second section, which is controlled to deliver the lead through the lower sections to the siphon intake at the bottom of the kettle at a temperature near the freezing point. The lower hearths may be fired occasionally when it becomes necessary to remove alloy accretions on the kettle sides and bottom.

Each of the continuous desilverizing units is capable of operating at any fixed tonnage between 8 and 16 tons per hr, producing lead containing about 0.02 oz of silver per ton.

The operating crew consists of an operator, an assistant operator, and three helpers. They are able to do all the work connected with the operation. Most of the time two of these helpers are free to be used for other plant work.

Dezincing

When the surge kettle following the continuous desilverizer is full, the lead is pumped to the dezincing kettles for treatment by the Harris process. This consists of circulating the lead through a bath of molten caustic soda contained in the Harris cylinders, converting the zinc to sodium zincate, which remains in the spent salts. The last traces of arsenic and antimony are also removed by the molten caustic.

The sodium zincate salts from the dezincing operation are granulated in water, which decomposes the salt to yield zinc oxide and sodium hydroxide. The zinc oxide is filtered out for shipment to a zinc plant. The caustic soda is regenerated by evaporation of water from the sodium hydroxide solution and stored for treating subsequent Harris charges.

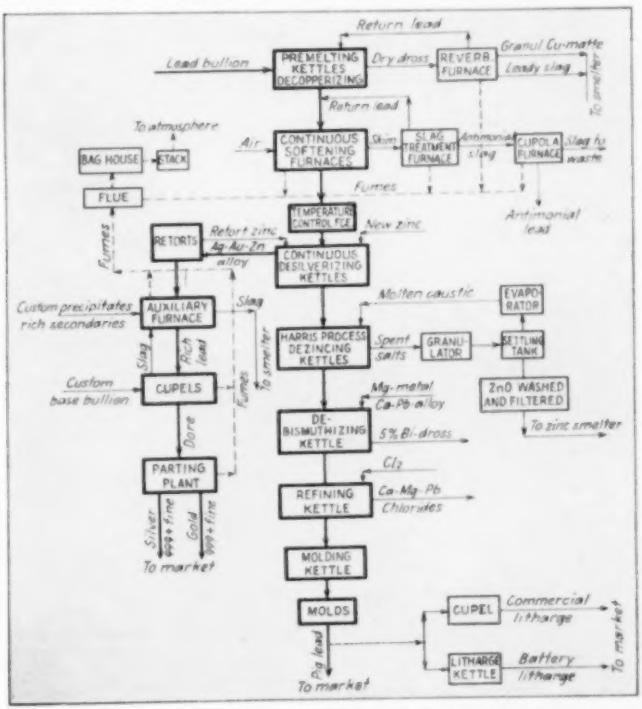
Debismuthizing

The dezinced lead is passed to a 200-ton kettle for debismuthizing by the Betterton process. It is mixed at low temperature with calcium lead alloy and magnesium metal and the bismuth is removed as a complex calcium magnesium bismuthide which rises to the surface as a leady dross. This dross, containing about 5 pct bismuth, is skimmed off and formed into blocks for shipping. The clean lead is pumped to a refining kettle. There the residual calcium and magnesium are removed as chlorides either with chlorine gas or by stirring with lead chloride. As a final step, the lead is stirred with a small amount of molten caustic to remove the last traces of impurities, and then is passed to a 250-ton receiving kettle for molding.

From the molding kettle the lead is pumped to a molding ring where it is cast into 100 lb standard pigs for market and stored or loaded into railroad cars, as the case may be. The transporting of the finished lead pigs is done with fork lift trucks.

Silver Concentration

The silver alloy obtained from the continuous desilverizing kettle operation containing approximately 60 pct Zn, 15 to 20 pct Au + Ag, 14 pct Pb, and 1 pct Cu, balance Zn, is charged to a battery of standard retorts in Faber Du Faure tilting furnaces. The zinc is distilled off and the condensate molded in zinc blocks to be returned to the desilverizing kettle. The residue of gold, silver, and lead is taken either directly to the silver concentration cupels or charged to a small auxiliary reverberatory furnace.



Lead refinery flowsheet of the Cia. Metalurgica Penoles, S.A. Over 7000 tons of bullion per month is currently being treated. Products and by-products resulting from the operations are:

- Speiss and matte (Cu)
- Antimonial lead
- Zinc oxide
- Pig lead
- Ca-Mg-Bi complex
- Bi dross
- Gold
- Silver
- Commercial litharge
- Battery litharge

These huge dezincing, debismuthizing, and molding kettles receive desilvered lead from the surge kettle in that order. The lead from the molding kettle is cast in 100 lb pigs for shipment.

from which the rich lead is tapped when needed to charge the silver concentration cupels.

In addition to serving as a surge furnace for the rich retort lead, the auxiliary furnace is used to melt custom precipitates and high grade concentrates. All cupel room secondaries, such as cupel barrings, sweeps and coppery-lead-oxide slags from silver concentration cupels, also are charged to this furnace for liquation. The slag formed in the furnace is run into pots, crushed, and shipped to the Torreon smelter.

The rich lead from the retorts and auxiliary furnace is charged to cupels for concentration to Dore, according to standard practices. The oxide slag from the cupels is run into pots and charged to the auxiliary furnace or shipped to the lead smelter as a cupel copper litharge. The Dore is refined in the cupel to a fineness of 996 using nitre and sodium carbonate and is then molded from the cupel into anode plates for electrolytic separation of gold and silver in the parting plant.

Parting Plant

The parting plant operates on the standard Balbach Thum process for electrolytic separation of gold and silver. The Balbach Thum cells used consist of cement tanks lined with a plastic compound and a graphite plate on the bottom. A wooden frame with a glass rod bottom supports a cloth lined basket into which the anode plates are placed. A silver-copper-nitrate solution is used as electrolyte. The

Silver crystals are deposited on a graphite plate in the Balbach Thum cells. The crystals are washed, melted, and molded into 1000 oz bars, shown ready for shipment.

silver crystals depositing on the graphite plate are periodically removed from the bottom of the cell. They are washed, melted and molded into 1000 oz fine silver bars of 999+ fineness for the market.

The gold remains on the cloth lining of the basket as an impure mud. This is taken out, digested with nitric acid to remove soluble impurities, melted and cast into anodes for refining by the Wohlwill electrolytic process. In this process the impure gold anodes are suspended in a porcelain cell containing gold chloride solution as electrolyte. Cathodes are made of pure gold foil on which the gold crystals form a firm deposit. A set of rolls is provided to prepare the gold starting sheets. The cathode is dried, melted, and the metal molded into commercial 400 oz bars for the market.

All slags, sweeps and dirty metals from silver refining and parting are returned to the cupels for retreatment and metal recovery.

General

Natural gas is used as fuel in all refinery operations. All nonladen combustion gases are collected in one flue system connected to a steel stack located inside the refinery building from which the gases go to waste.

The laden fumes are collected in a separate flue system which is connected to a 700 ft long flue leading to a baghouse operating with 4 sections of 150 bags each. A brick stack discharges the filtered clear gases to the atmosphere.

Electric power is produced at the company's own steam-electric plant which is operated under the supervision of the mechanical dept. A large machine shop, electric shop, and carpenter shop take care of all plant maintenance, repair work and new construction.

Switching of railroad cars inside the plant and from and to the yards of the National lines is accomplished with a company-owned steam locomotive and its switching crew.

A well equipped chemical laboratory takes care of all analytical work for plant control as well as check and control samples from other units and outside departments of the company.

The Monterrey plant is operated by a crew of approximately 500 workmen and a staff of 15 employees in addition to the necessary clerical force.

Steel Mill Instrumentation Improves Production and Quality

by L. W. Heinzinger

AN evaluation of instrumentation must be aimed at helping the metallurgist establish safe operating limits and develop improved methods. The field of quality and material control has greatly expanded during the last ten years. A set of operating standards giving ideal conditions, from a metallurgical standpoint, can be established by using choice scrap and a high percentage of pig iron. The metallurgist, however, is confronted with the problem of charging less costly types of scrap in maximum permissible amounts, while still turning out a satisfactory product. He also must adjust his thinking and quality practices to high production rates at the open hearth and rolling mills. His methods must be directed toward developing the maximum possible yield from the ingot.

The four factors that influenced the adaptation of instrumentation to the metallurgical control processes at Bethlehem Pacific Coast Steel Corp. were material cost, production rates, yield, and quality.

The principal raw material in making steel by the cold-charge process is scrap. During the last ten years a marked change in the character and relative value of scrap receipts has taken place. The sharp upward trend in pounds of coke per ton of ingot needed to meet the carbon requirements is shown in Fig. 1. This trend can be attributed to two main causes:

1—Steel is used in ever increasing amounts as sheets, and this low carbon material is returned to the steel producers in the form of bales.

2—Cast iron previously had lower market value than scrap, and dealers made little effort to segregate it. Now cast iron has greater market value, and as a result, little of this higher carbon melting material is contained in normal scrap receipts.

The change in scrap composition resulted in a need for greater thermal loads, accomplished by burning more oil per hour on open hearth furnaces, to maintain production rates. It is necessary to consider this in evaluating the effect instrumentation has on oil consumption. This installation of instrument control at the open hearths of Bethlehem's Seattle plant was made during the same period this change in scrap character took place.

Open Hearth Instrumentation

Substantial savings on fuel were anticipated at the initial runs on the open hearth furnaces. When good results were not forthcoming, a number of variations in furnace operation were tried. These practices were reflected in lower production rates and quality troubles which invariably accompany inconsistent furnace operation.

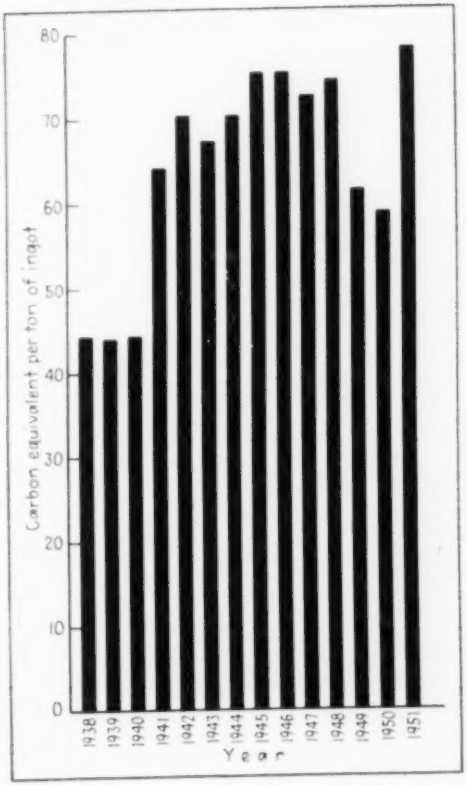


Fig. 1—Increasing use of low carbon sheets and decreasing use of high carbon cast iron are responsible for the upward trend in coke needed to meet carbon requirements.

Efforts to effect fuel economies apparently put the cart before the horse. With these results as a guide, furnace operation was standardized at instrument values considered good from the experienced fur-

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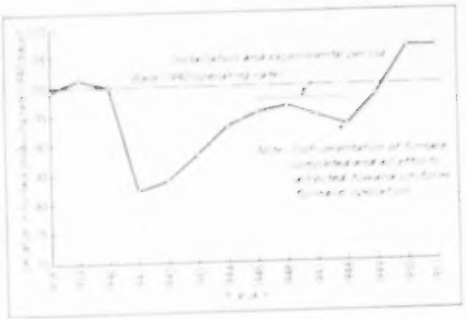


Fig. 2—Production increased markedly with the completion of furnace instrumentation in 1948. Instrumentation permits the furnace operator to assess all variables, and run at maximum safe operating limits.

nace operator's standpoint. This involved a sharp, fast melting down flame, and a higher air-fuel ratio than desired from straight thermal considerations. Thus instrumentation was used as a tool to implement open hearth supervision, not to supplement it. On this basis, considerable improvements were achieved in furnace operation. Specific gains attributed in part or fully to instrumentation were: 1—Increased production; 2—improved quality; and 3—improved yield.

The marked increase in production, shown in Fig. 2, was accomplished in part because instrumentation eliminated the blind spots in furnace operation and allowed proper assessment of the quality of scrap on furnace operation. This scrap evaluation was an important factor. From a consideration of melt down time and charging time of light and heavy grades of scrap, an optimum scrap density of 3800 to 4500 lb per cu yd was determined. When the average charge density is outside these values, the open hearth is penalized by longer heats. The light scrap uses longer charging time, and the denser scrap delays the heat because of increased melting time.

Instrumentation also provided an unbiased umpire for all types of furnace operations. An accurate charting is made 24 hr a day. The personal element of varied types of operation from shift to shift has been practically eliminated. Roof temperatures, checker temperatures, furnace pressure, and air-fuel ratio are indicated at all times, enabling the individual furnace operator to run at the maximum safe operating limits. This uniformity factor in furnace operation provides an excellent opportunity to assess benefits attained, both in ingot quality, and production by satisfactory melt-in carbons. Losses in production resulted from low or high furnace melts. In heats melting low, furnace production dropped 7½ pct. In those melting high, production was reduced about 9 pct. Similarly, on the heats melting low, the incidence of off-grade was twice that of heats having satisfactory carbon melts, and over twice the incidence in off-grade with high melts.

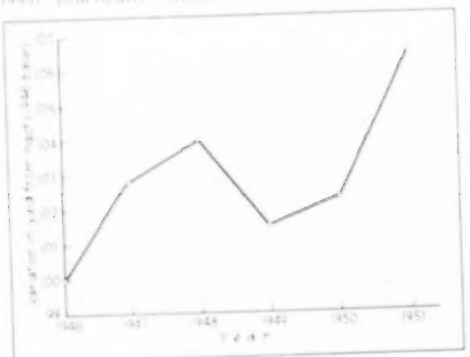


Fig. 3—Refinements in the steelmaking process, and accurate evaluation of the ingot produced, both afforded by instrumentation, are responsible for the improvements in quality and yield. This graph summarizes experience at one of the rolling mills at the Seattle plant.

The advantage of having uniformity in melts is obvious and shows furnace operation can contribute to this to a considerable degree. Therefore, standardization in furnace operation will allow adjustments to be made in carburizing material to give satisfactory melts. Any marked change from this then can be attributed to scrap, and insistence on greater uniformity of furnace charge can be made. The ability to reduce the operating variables to a minimum and to identify a problem that has developed with a specific step in a control process is most helpful to the metallurgist.

The user of steel, in many instances, can not relax quality requirements. With the progressive change in physical and chemical characteristics of available raw materials, this condition is of paramount importance to 100 pct cold charge shops. Only by carefully evaluating all factors affecting ingot quality and diverting questionable heats to less restrictive grades can satisfactory operating experience be maintained. Instruments installed to supply many of the needed answers were:

1—Bath thermocouple for heat temperature prior to tap.

2—Optical pyrometer for pouring temperatures.

3—Magnetic carbon analyser for tapping carbon. This is important in evaluating the rimming action of heats.

The use of instrument controls resulted in improvements in the quality and yield of the finished product. A graphic summary of experience on one of the Seattle plant rolling mills is given in Fig. 3. This can be attributed to refinements in the steelmaking process and a more accurate evaluation of the ingot produced. This can be done only if accurate, unbiased information that instrumentation affords is available.

Rolling Mill Practice

In the rolling mill, as in the open hearth, reheating furnaces were completely instrumented. The metallurgical benefits of these installations closely paralled those in the open hearth. A complete recording of the temperature of the ingot on the furnace hearth and at the billet shear is available.

Since this particular practice has been in effect, practically no instance of burned steel has occurred. Furthermore, control of the air-fuel ratio (less excess air) improved the surface of the rolled product. This was accomplished in spite of increased copper content in the available raw materials. Copper, if not controlled within maximum limits, may result in increased surface checking because of differential oxidation.

The exacting requirements of steel users make it mandatory that a complete record be kept of rolling

Fig. 4—Rolling temperatures are accurately recorded by the radiation device at the upper right sighting on the billet. The radiation pyrometer is mounted on a conveyor with the recording chart, which is visible to the heater and roller.

temperature of the finished product. This is especially true of the chromium, nickel-chromium and nickel-molybdenum steels being produced. Full benefit of the alloys are not developed unless they are rolled as close to the critical range as possible. For this purpose the recording chart and radiation device mounting in conveyor, Fig. 4, is a very practical tool. Not only is a permanent recording made but the dial is visible both to the heater and roller. Rolling temperatures also can be varied to control the tensile properties. This can be helpful in the application of somewhat lower carbon steel to structural sections, where by rolling at lower finishing temperatures, increased tensile properties are produced. In producing steel to grain size, the finishing temperature of the bar is important and cannot effectively be controlled without permanent temperature recording equipment.

The success of any instrumentation program is dependent on the recorded measurements being representative of existing conditions. This is particularly true of temperature measurements. It was found that the heaters on reheating furnaces have been able to do a better job by having temperature measured at three different points: 1—Point of discharge; 2—junction of soaking and heating zone; and 3—start of main heating zone. With this type of installation, shown in Figs. 5 and 6, it is possible to progressively follow the rate of ingot heating through the furnace, and the proper relationship between the different zones can be maintained. It is essential for full utilization that control equipment be maintained in good working order, and daily checks made of the control points.

Instrumentation has proved to be a useful and necessary tool for the metallurgist. It gives accurate unbiased information 24 hr a day, 7 days a week, and allows for accurate evaluation of the metallurgical processes performed in steelmaking and rolling. Before the installation of the various instruments, many factors which affect quality and production could not be properly quantitatively evaluated, and corrective measures were often uncertain. The installation of controls on both open hearth and reheating furnaces provided operators with more dependable information on what is taking place during operations. This has not lessened the responsibility of their jobs, but actually required more skill. With this added accurate information available, both improvement in quality and increase in production can be expected.

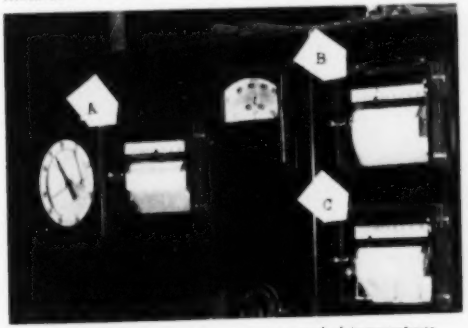


Fig. 5—A permanent and continuous record of temperatures at three different points of the reheating furnaces is kept. Charts A, B, C, record temperatures at similarly marked points on Fig. 6, discharge end, soaking and heating zone, and main heating zone.

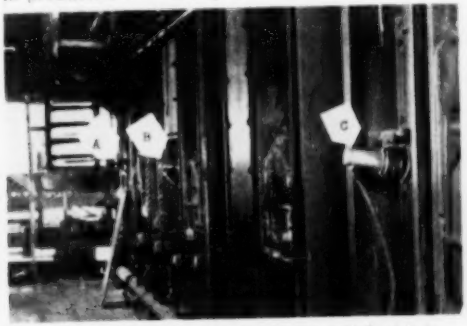
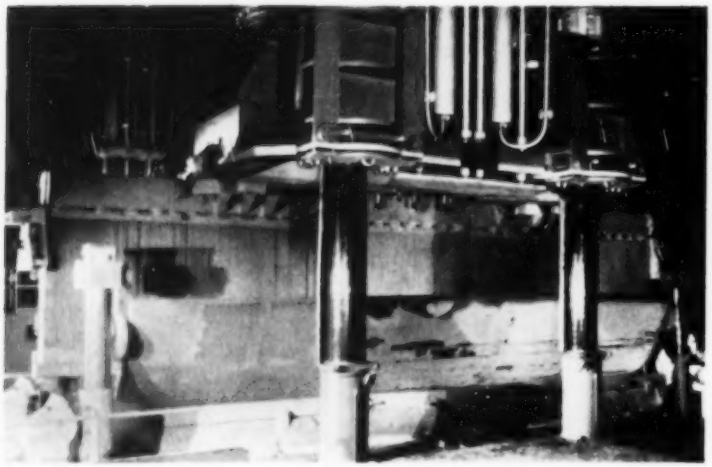


Fig. 6—By maintaining three temperature control points in the reheating furnace, temperatures representative of existing conditions are obtained. The radiation devices sight on the top of the ingot with a slight angularity, essential for correct measurements.



A 6 in. thick steel plate, the heaviest ever rolled, is being formed into a boiler drum section in this new vertical press at B & W. The operation, performed at 1850 F, takes about 20 min. A special furnace, 14 x 50 ft, was constructed to heat the plate to forging temperature.

B & W'S Giant Press Forms Heavy Plate, Pierces Ingots For Hollow Forgings

BENDING of the heaviest steel plate ever rolled — a sheet 6 in. thick, 36 ft long, and 10 ft wide — was accomplished at the Babcock & Wilcox Co. tanker div. at Barberton, Ohio. Making this feat possible was the 6500-ton hydraulic press built and installed at the plant. The press is also used to pierce ingots for subsequent processing into rough hollow forgings on a 1200-ton horizontal draw bench. This hydraulic draw bench, with its 30-ft stroke, is unique in this country. The press and draw bench, designed by Hydropress, Inc., were constructed at a cost of $2½ million, as part of the $30 million expansion program of B&W.

The huge slab of steel, weighing 87,000 lb and called at 87000 was produced by Lukens Steel Co., Coatesville, Pa., and was press formed at 1850 F. The B&W press can handle sections up to 42 ft long, 12 ft wide, and 7 in. thick. Boiler drums for high duty central station units are fabricated by welding a number of sections formed from heavy plate, and the number of plates used has a direct bearing on the time and cost of fabricating a drum that can run over 80 ft long. The 42-ft sections that can be produced on the press will cut the number of circumferential welds needed from 10 to 3. The result will be substantial savings, not only in fabrication, but in X-raying welds for soundness. In addition, utility companies will be able to hold down costs by using high temperature-high pressure steam in boilers designed around the heavier sections available.

In producing hollow forgings, the same press is used to pierce hot ingots. The hollow ingot is then fitted over a mandrel on the horizontal draw bench, the largest in this country constructed for this purpose. With the mandrel holding inside dimensions, the hot ingot is forced through a series of ring dies, reducing the outside diameter and increasing its length, until desired dimensions are obtained. Forgings up to 35 in. OD with 4½ in. walls, and up to 22 ft long have been produced by this method. Various shaped mandrels and dies can be used on the draw bench to provide square, rectangular, oval, or other cross-sections.

Thick walled hollow forgings are needed to produce the headers in modern central station boilers, which must withstand successively higher temperatures and pressures in keeping with design trends. Water walls, economizers, and super heaters in a single boiler may require as many as 30 headers.

Until the advent of the B&W hydraulic press and draw bench combination, the headers were produced by forging solid ingots and then boring out the centers. Although first considered only for boiler parts, the wide range of specifications possible make the hollow forgings adaptable for other industrial uses. Chemical and process industries may use them in accumulators, pressure vessels, rolls, etc. They may also be suitable as bearing races in ball bearings, and in the petroleum industry for high pressure oil and gas separators or high pressure heat exchangers.

The normal operating capacity of 6500 tons of the vertical hydraulic press will be increased to 8500 tons when an intensifier is added. Operating pressure is 3000 psi. The press has a daylight of 20 ft and an operating stroke of 9½ ft. A 500 ton ram, 22 in. diam, with a 54 in. stroke, used for piercing ingots, is located on the press center and in the pit below the bottom platen. The ram is fitted with two return cylinders. The matrix used for piercing is fitted with an ejector ram with an 8½ ft stroke. The three 45 in. diam main cylinders can be operated

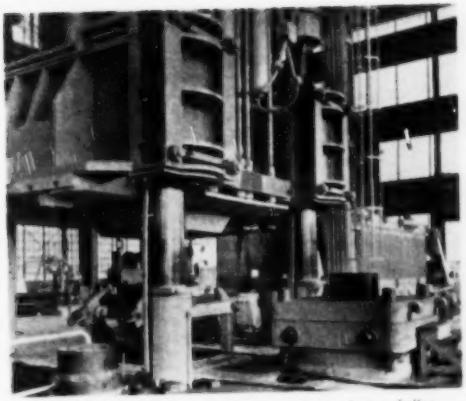
singly or in combination, providing 2100, 4400, or 6500 ton steps.

When functioning as a piercing press, the heated billet is loaded into the matrix and the stripping plate installed while the matrix is positioned on a shifting table 14 ft from the center of the press. The shifting table then moves the loaded matrix into working position. Billets up to 26,000 lb can be handled. After piercing, the shifting table returns the matrix to its former position where the ejection cylinder functions to unload the workpiece.

In forming drum shell plates on the press, the piercing matrix is moved out of the way and to the rear of the work area. This leaves an unobstructed space between press columns for the entry of the hydraulically operated plate manipulator which moves the workpiece from its loaded position to its working position under the moving platen. This plate manipulator, which comprises the 42 ft long lower bending beam, also forms the carriage for cross travel through the press. Four hydraulically operated manipulators, two on either side of the carriage, handle the workpiece. Any two manipulators are capable of handling a 50-ton plate. Angular tilt of the manipulators of approximately 20° from vertical to the edge of the beam is accomplished with cross cylinders located on the carriage. All motions connected with the manipulator are hydraulically controlled.

Plates up to $2\frac{3}{4}$ in. thick are cold pressed. Heavier plates are rough formed while at forging temperature, then finish formed at room temperature.

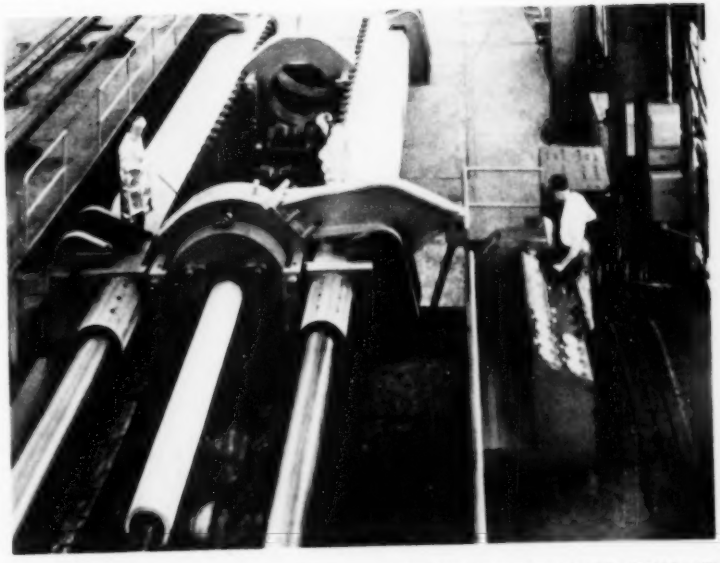
The horizontal draw bench utilized for forming the hollow forgings has a 600 or 1200 ton forward stroke 30 ft in length, with a return stroke operated at 600 tons. The unit has an overall length of 114 ft and a 32 in. bore main cylinder. The die bed is $31\frac{1}{2}$ ft long, with location for die holders along 28 ft of its length. The unit is equipped with swivel type die holder and 7 roller supports. As ring dies on the draw bench can be changed quickly, one or two lengths of a particular size, shape or thickness of a hollow forging can be produced at low unit cost per forging for the change-over, thus providing great flexibility in manufacturing operations.



Piercing of hot billets, the first step in producing hollow forgings, is also done by this versatile press. For this operation, plate manipulator is moved out of way, and the piercing matrix swung into position

The hydropneumatic pressure system for operating the press and draw bench is powered by three triple piston single stage pumps, each geared to a 500 hp, 2300 v synchronous motor. The large pressure storage capacity required is provided by an accumulator plant comprised of two water and five air bottles of the company's normal banded vessel construction.

To provide greater flexibility, an additional furnace for reheating hollow forgings is in the process of installation. Work has also begun on a self-contained melting shop including a new arc furnace, to insure an adequate supply of ingots. A special furnace, with inside dimensions of 14x50 ft, with a 7 ft ceiling, was constructed for heating the plate and ingots to forging temperatures.



The pierced ingot is converted into a hollow forging of specified dimensions in this giant sized horizontal draw bench. Depending on the desired finished size, one to several passes through different sized ring dies may be necessary. Reheating of the ingot usually is called for after two or three passes.

The Metallwerk Plansee, where the First Plansee Seminar was held, is set amidst the beautiful Austrian Tyrol at Reutte.

Powder Metallurgists At Austrian Seminar Discuss —

New Sintered Aluminum Powder Tungsten and Molybdenum Silicides

ALUMINUM of superior strength and particularly high temperature characteristics, produced through the use of a very fine, pure, superficially preoxidized powder, was reported at the first Plansee Seminar, "De re Metallica," held at Reutte, Tyrol, June 22 to 26, 1952.

Three hundred representatives from 17 Western nations showed considerable interest in the paper presented by A. von Zeerleder. The powder was prepressed cold at 14 to 35 tsi, sintered at 500° to 600° C, then hot pressed at 35 tsi and finally extruded at 500° to 600° C at a pressure of 35 to 70 tsi. The extruded material can be die forged or hot swaged. The extrusion step, however, may be omitted, and the hot pressed material die forged directly. The product exhibits tensile strength values in excess of 50,000 psi. The creep strength at 400° C as well as the high temperature fatigue strength of the pure aluminum SAP material are superior to those of all known aluminum alloys. Although rather expensive, SAP appears to open important new applications for aluminum products in the temperature range of 200° to 400° C.

The meeting was sponsored by the American Electro Metal Corp., Yonkers, N. Y.; Metallwerk Plansee, Reutte, Tyrol; and Metro-Cutanit Ltd.,

Paul Schwartzkopf, left, president of American Electro Metal Corp. and organizer of the Seminar, chats between sessions with Henry H. Hausner, manager of atomic energy engineering, Sylvania Electric Products, Inc.

London; and organized by Paul Schwartzkopf. Scientists and industrialists working in the field of powder metallurgy met with physicists and chemists interested in theoretical fundamentals.

The first of the three series of lectures was on Physical and General Metallurgy. F. Skaupy presented *Present Views on the Nature of Metals*; A. G. Smekal, *Ideal and Real Crystals*; H. Nowotny, *Bonding in Intermetallic Phases*; G. M. Schwab, *Electron Theory of Mechanical Strength*; H. Forestier, *Effect of Adsorbed Gases on the Reactivity of Metallic Surfaces*; and M. Auwarter, *Stability of Inorganic Compounds in High Vacuum*. Special attention was centered on the paper by W. Seith on *Diffusion in Metals*. In this review of modern concepts of diffusion, the author contended that the effect of pore formation attributed to different diffusion rates of the components will undoubtedly enforce a revision of the basic concepts of the diffusion mechanism.

The experimental evidence presented by Seith was supplemented by H. Buckle with color slides. The mechanism of pore formation, that is, the *coagulation* of vacancies to microscopic pores was of special interest to powder metallurgists since it may be considered as a reversal of the mechanism of pore elimination during sintering. Discussion of this paper made it clear why pore formation by different diffusion rates was not noticed earlier. The existence of the pores, although observed previously, was incorrectly attributed to the original contact boundary. It was the spacer technique of Kirkendall that permitted the demonstration that the location of the pores does not coincide with that of the boundary.

During the series on Hard Metals, R. Fitzer summarized his work at the Technical University Vienna, on the development of high temperature materials by silicizing tungsten and molybdenum. Following this presentation, R. Kieffer demonstrated two types of new heating elements developed at the Metallwerk Plansee. The first type consisted of loops of silicized molybdenum, while the second represented bars of compacted molybdenum silicide. The molybdenum silicide exhibited considerable mechanical strength and resistance to thermal shock, and permitted operating temperatures of 1700° C. The discussion indicated that this development is expected to play an important part in future developments of furnace construction, particularly in furnaces for the ceramics industry.

Other papers presented were *The Ternary System W-C-Co*, by J. T. Norton; *Preparation of Pure TiC*, by G. F. Hüttig; *Solid Solubilities at 1250° C of Various Carbides in the Bonding Metals Co, Ni, and Fe*, by T. Raine and R. Edwards; *Systematics of Properties of Hard Metals*, by C. Ballhausen; and *Ternary Systems Me.-Me.-B, and Relative Strength of the Bond Between Transition Metals and Boron*, by R. Kiessling.

At the final session, lectures were given by G. J. Comstock and F. H. Clark, *Development of High Strength Heat Treatable Products from Alloy Powders*; H. S. Cannon and F. V. Lenel, *Mechanism of Liquid Phase Sintering*; A. Langhammer, *Powder Metallurgy as viewed by a Manufacturer of Metal Powder Products*; G. Ritzau, *Thermoelectric Analysis of the Sintering Mechanism*; E. M. Onitsch-Modl, *Analysis of Alloy Formation During Sintering by Microhardness Testing*; and H. H. Hausner, *Effect of Lattice Changes on the Sintering Process*.

Speaking for the guests, G. F. Hüttig of the Technical University Graz, thanked Dr. Schwartzkopf for the organization of the Seminar. "The seminar has sintered together the powder metallurgists of the free world to one family," he declared, "and the established close cooperation will undoubtedly largely contribute to further progress in our field."

AIME Fall Meeting at Centennial of Engineering

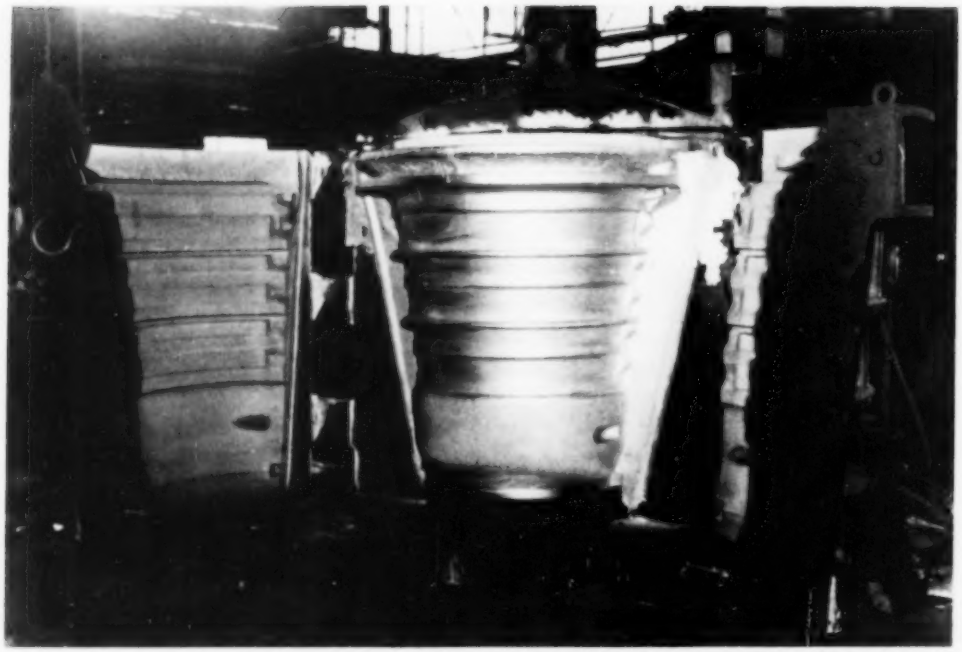
THE Fall Meeting of the AIME—to be held in conjunction with the Centennial of Engineering—will be held in Chicago. Sessions of interest to members of the Metals Branch will take place Sept. 5 to 9, 1952, and Mining Branch sessions begin September 3. Headquarters hotel will be the Palmer House. A paper on the *Growth of AIME* by A. B. Parsons will be given Wednesday, September 3 at the Eighth Street Theater.

The Iron & Steel Div. will hold a session at 2 pm Friday, September 5, in the Crystal Room of the Palmer House. Two papers are scheduled for this session: *Developments in Steel Alloys*, by Elmer Gammeter, Director of Globe Steel Tubes Co. Laboratories; and *A Review of Wide Strip Rolling*, by D. S. Holstein, general superintendent of rolling and finishing, Middletown div., Armco Steel Corp.

Friday evening at 6:30 pm, the Chicago Section, AIME, will hold a dinner meeting at the American Bar Assn. headquarters in the Equitable Bldg. E. C. Bain, vice-president, research and technology, U. S. Steel Co., will be the speaker at this meeting.

An AIME Dinner Dance will be held at 7 pm Saturday evening, in the Red Lacquer Room of the Palmer House. The AIME Board of Directors will hold a meeting Sunday afternoon from 2 to 5 pm in the Crystal Room of the Palmer House.

On Monday and Tuesday, September 8 and 9, although not part of the AIME program, a Mineral Industries Symposium sponsored by the Centennial will be held in the Ballroom of the Hotel Sherman. Clyde Williams, Battelle Memorial Institute, will be chairman for this meeting, and R. J. Anderson, Battelle Memorial Institute will be secretary. After an *Introduction* by the chairman, the following subjects will be discussed: *Exploration for Metals, Petroleum and Water*, W. E. Wrather, U. S. Geological Survey; *Mining and Quarrying*, D. H. McLaughlin, Homestake Mining Co.; *Coal Mining, Preparation, and Utilization*, J. B. Morrow, Alford Morrow & Associates; *Ore Beneficiation and Hydrometallurgy*, O. C. Ralston, U. S. Bureau of Mines; *Nonmetallic Materials*, J. D. Sullivan, Battelle Memorial Institute; *Iron and Steel Production and the Coke Industry*, Walther Mathesius, Freyn Engineering Div., Koppers Co., Inc.; *Nonferrous Smelting and Refining*, R. W. Diamond, Consolidated Mining & Smelting Co. of Canada, Ltd.; *Synergism of Engineering and Petroleum*, R. E. Wilson, Standard Oil Co. (Ind.); *Role of Metals in Our Economy*, Zay Jeffries, General Electric Co.; and a *Commentary* by Clyde Williams.



The largest permanent mold aluminum casting, 65 in. high, 45 in. diam, weighing 500 lb was produced by Harsh Bronze & Foundry Co., Cleveland. Meehanite molds were used.

Many Mechanisms At Work Producing Grain Refinement In Light Metals

by Harold Bernstein

THE problem of grain refinement is essentially that of the liquid-solid transformation. Despite its fundamental nature and its familiarity, it is attended by a good deal of controversy. There is agreement on the general principle that solidification occurs by a nucleation and growth process. Disagreements arise because of the physical difficulties in identifying the nucleating particles and their mode of development. Information about nucleation and growth is derived from melt chemistry, its thermal history and the structure of the resulting solid.

The classic approach to solidification is embodied in the principles of Tammann.[1] He proposed that the grain size of a cast metal is a direct consequence of the rate of formation of nuclei, Nc, and the velocity of crystal growth, Vc. These factors apply in the absence of preexisting nuclei, i.e., the melt is assumed to be perfectly homogeneous. The Nc factor is sensitive to the cooling rate. The Vc factor is influenced by the temperature and physical characteristics of the melt.

If it is assumed that nuclei are present, then as cooling progresses, the nucleus grows by adding material from the molten reservoir. The initial development of the solid is idiomorphic. Its final shape, however, is determined by thermal and concentration gradients, and the pressure of neighboring crystals. In the light metals, the grains are visible to the unaided eye, after suitable surface preparation. Their size may vary from coarse columnar grains to fine equiaxed grains with a diameter of 0.007 in. Various grain structures in aluminum and aluminum alloys may be seen in Fig. 1. Elementary aluminum of high purity, 99.997 pct, tends to have a columnar structure, which may be coarse or fine, depending on the rate of cooling in the mold. The binary alloys usually have an equiaxed grain structure. On the simple basis of percent weight needed

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to accomplish refinement, they may be classified into two groups. In one group, substantial amounts of alloy are required and this includes the commercial casting alloys like aluminum-magnesium, aluminum-copper and aluminum-zinc. In the second group, only traces of alloying element are used, like titanium, columbium, boron. The latter are of experimental interest only. Distinct mechanisms of refinement have been suggested for each group. Refinement by restriction of crystal growth in the first group, and refinement by active nucleation in the second group.

Theories of Growth Restriction

In the binary alloys, solidification occurs over a range of temperature. As soon as the first solid forms, the liquid around it becomes impoverished or enriched in the alloy, and consequently has a lower melting point than the liquid near the center of the casting, which is of average composition. The growth of the initial solid is thereby restricted and additional solidification occurs when the liquidus isotherm moves to liquid of average composition. The process is repetitious and an equiaxed grain structure is the result. This constitutes the concentration gradient theory as postulated by Northcott in 1938. Northcott's experimental work was done on copper. More recently, Eborall[7] and Cibula[8] have applied this theory to aluminum. They attempted to express the theory in semi-quantitative terms, by relating the refining potential to the composition interval between the initial solid and the residual liquid, and the slope of the liquidus curve. Thus, systems showing small differences in composition between the initial solid and the residual liquid will have fine grains, provided diffusion does not wipe out the concentration gradient.

This yardstick appears to be applicable to systems whose liquidus-solidus curves have a positive slope at the aluminum-rich end of the constitution diagram. Examples of such systems are aluminum-titanium and aluminum-zirconium. The common binary alloys like aluminum-copper and aluminum-zinc have negative liquidus-solidus slopes in the same area, and attempts to apply the yardstick have not been successful. For example, in Fig. 2, a portion of the aluminum-copper constitution diagram has been superimposed on the grain refinement curve for the same alloy. It is apparent that the length of the composition interval increases with copper content, although the grain size decreases. There does not appear to be a relation between the average slope of the liquidus curve and refining potency for the systems given in Table I. There are, of course, exceptions.

The Adsorption Effect

It is interesting to note that Northcott advanced an alternate, and to him, more attractive theory, to account for the crystallization of copper, the adsorption effect. This effect is attributed to the adsorption of solute atoms on the surface of the growing crystal. The attractive forces exerted by the solid surface are satisfied by this process, so that the adsorbed surface offers little attraction to the attachment of additional atoms. The binding power

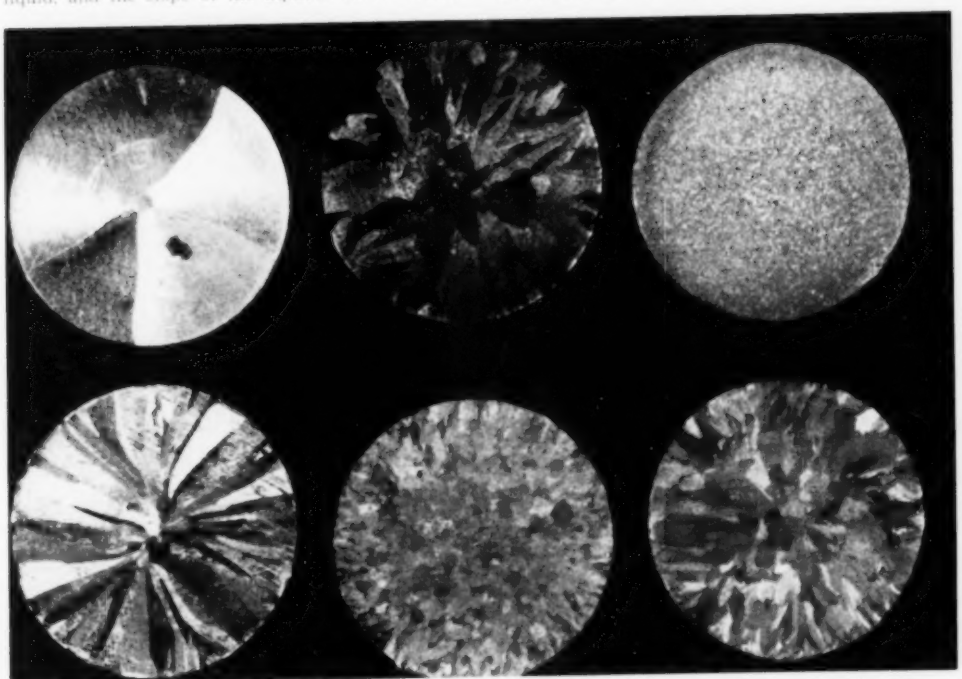
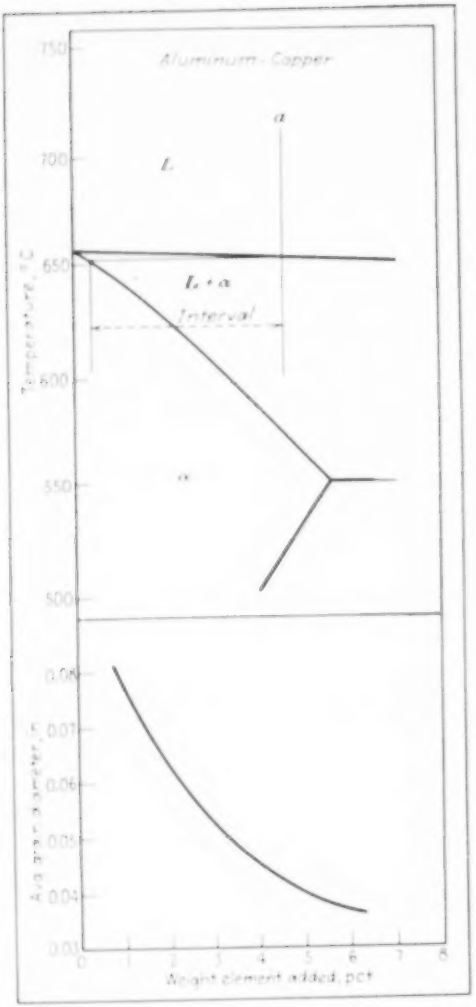


Fig. 1—Various grain structures in aluminum and aluminum alloys. High purity aluminum (99.997 pct) tends to have a columnar structure, while binary alloys usually have an equiaxed grain structure.

Top	H.P. Aluminum	H.P. Al-4.40 pct Cu	H.P. Al-0.23 pct Ti
Bottom	H.P. Aluminum	C.P. Al-4.18 pct Cu	C.P. Al-6.12 pct Zn



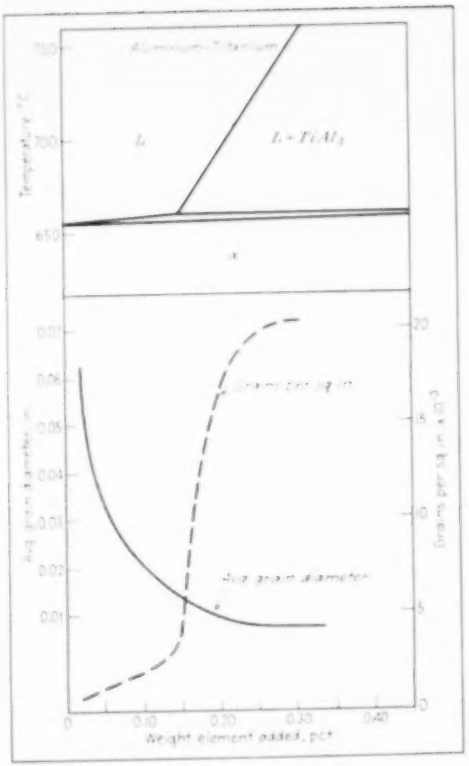


Fig. 3 (above)—In the Al-Ti system, the peritectic reaction begins at 0.15 pct Ti. When grain refinement curves are superimposed, it can be seen that changes in slope coincide with the onset of the peritectic reaction.

Fig. 2 (left)—Part of the Al-Cu constitution diagram is shown superimposed on the grain refinement curve for the same alloy. It can be seen that the length of the composition interval increases with copper content, while grain size decreases.

of the adsorbed atom and its subsequent growth restriction effect was related in an empirical way to its valence. While the general nature of the theory was considered satisfactory in the discussion that followed, objections were raised by Hume-Rothery concerning the extension of the valence characteristics of the free atom into the liquid or solid state.

The Effect of Surface Tension

This phenomenon was investigated by Bastien in 1940. He made surface tension measurements on high purity aluminum and a series of alloys, including Mg, Fe, and Si. Bastien found that high purity aluminum had the highest surface tension and the coarsest grain size, and the 7 pct magnesium-aluminum alloy had the lowest surface tension and the finest grain size. He deduced that surface tension acted to restrict the growth of the nucleating particles. The effect of impurities on the velocity of linear crystallization was considered to be negligible.

It is probable that these factors promote grain refinement to some extent. However, a significant part of the refinement in the binary alloys is contributed by impurities, as may be seen in Fig. 1, center. This is more strikingly demonstrated by superheating, which converts an equiaxed grain structure into a coarse columnar one. The nucleation factor appears by far to have the greater weight in grain refining. There are two types of nuclei, depending on their origin: Kindred nuclei which are formed from the principal components of the melt, and foreign nuclei which arise from impurities or combinations of impurities and melt components.

Nucleation Theories

Spontaneous Nucleation. In a homogeneous liquid, nuclei are formed spontaneously in response to the rate of cooling. The rate of cooling of the melt affects the extent of undercooling, which creates a condition of acute instability in the liquid and ac-

celerates the formation of nuclei. Measurements of cooling rates in high purity aluminum have been made by Kondic and Shutt[6] who reported increasing refinement with increases in the extent of undercooling. The effect of rate of cooling on the structure of high purity aluminum may be seen in Fig. 1. The top specimen was cast in a permanent mold at 595°C (1100°F), and the bottom one at 400°C (750°F). The effect of the increase in cooling rate was to refine the columnar structure.

Cibula made cooling rate measurements on the aluminum-8 pct copper alloy and found undercooling at both the surface and interior of castings. While this will yield a finer equiaxed grain size in the interior of the casting, the periphery will be columnar.

Nucleation by Intermetallic Compounds: Active grain refinement by the addition of small amounts of certain elements was associated with the appearance of a peritectic reaction by Iwase, Asato, and Nasu[7] in 1936. Working with the alpha alloys of copper, they noted a sudden reduction in grain size, when the concentration of added element, Fe or Co, reached a value corresponding to the beginning of the peritectic transformation.

The mechanism of the peritectic reaction may be understood by consulting the constitution diagram, Fig. 3. For example, in the aluminum-titanium system, the peritectic reaction begins at 0.15 pct Ti. Consider an alloy of 0.25 pct Ti at a temperature of 760°C (1400°F), at which temperature the alloy is molten and homogeneous. Upon cooling to the liquidus temperature, $TiAl_3$ precipitates out and continues to precipitate until the eutectic temperature is reached. At this point, a reaction occurs between the primary solid and liquid peritectic composition:

$$L + TiAl_3 \rightleftharpoons \text{alpha solid}$$

Under cooling conditions this reaction will proceed to the right and the primary solid resorbed to form alpha solid solution. The advocates of peritectic refinement claim that this reaction either fragments the $TiAl_3$ into nucleating particles, or that the alpha solid solution formed is composed of fine crystallites which seed the melt. Refinement will occur at certain concentration levels which coincide with the beginning of the peritectic reaction. Recently, this theory found support in a paper by Crossley and Mondolfo.[8] They investigated a series of aluminum alloys with Ti, W, Mo, Zr, and Cr, all of which undergo peritectic reactions. Their experimental procedure consisted of preparing melts at temperatures 100° above the liquidus, measuring the grain size of the solid, and plotting grains per square centimeter against percent weight of added element. The grain refinement curves are shown in juxtaposition with the constitution diagrams in Fig. 3, and changes in slope appear to coincide with the onset of the peritectic reaction.

Serious objections have been raised as to the validity of this explanation. For example, Eborall reported marked attenuation of grain refinement by superheating aluminum-titanium alloys. Cibula coarsened the same alloy by passing nitrogen through the melt. If the nucleating particles are formed during the freezing cycle, as claimed, then operations of this type carried out prior to cooling should be innocuous. In addition, there is some question about the effectiveness of chromium as a grain refiner. It has been reported as having no effect on the grain size of aluminum.[9,10]

Table I. Relation Between Slope of the Liquidus Curve and Refining Potency

System	Average Liquidus Slope, °C per Wt Pct	Order of Potency[11]
Al-Mg	−6.6	1
Al-Cu	−3.4	2
Al-Zn	−2.0	3

Boron is an active grain refiner when added to aluminum or its alloys. The precise nature of its constitution diagram is in doubt, but it was reported by Mondolfo[9] to have a eutectic near the 100 pct aluminum ordinate. The grain refining effect of boron was attributed by Cibula to the formation of AlB_2 intermetallic compound, which nucleated the melt. Cibula reported further that the refining effect of boron was unimpaired by superheating, which is consistent with the above explanation.

Nucleation by Foreign Particles

While the theory of refinement by superheating has been proposed for magnesium base alloys containing aluminum, its general features are of interest. Fox and Lardner[10] discussed this in 1945. The mechanism of superheating consists of raising the melt temperature a significant amount, then cooling to the normal pour temperature. This produces a finer grain size than is obtained without superheating. Since superheated melts exhibit no undercooling, the nucleating particles are presumed to be foreign, that is, are formed from impurities in the Al-Mg alloy at the superheat temperature. They maintained that a superheating temperature of 1400°C (2550°F), is effective for aluminum, but presented no supporting evidence.

DePierre and Bernstein[11] conducted an investigation on grain refinement in commercial purity aluminum in 1949. Their experimental conditions paralleled those of Crossley and Mondolfo, except that melt temperatures were held constant at 730°C (1350°F). Results were reported in terms of average grain diameter. The left hand side of the aluminum-titanium constitution diagram and the corresponding grain refinement curves appear in Fig. 3. It may be seen that the plot of average grain diameter vs weight concentration yields a smooth curve, (solid line) with most of the refinement occurring prior to the beginning of the peritectic transformation. If these data are converted into grains per square inch and replotted, the curve (broken line) breaks sharply in the neighborhood of the peritectic transformation. In the case of titanium, this coincidence appears to be mathematical rather than physical.

However, thresholds were encountered by DePierre and Bernstein for the elements zirconium, tungsten, and molybdenum. The grain refinement curve for zirconium may be seen in Fig. 4. It is possible, therefore, that the peritectic transformation plays a part in grain refinement. Because of its many inadequacies, however, its role cannot be considered dominating. Considering the high melting points and limited solubilities of the elements involved, DePierre and Bernstein concluded that these elements participated directly in the formation of stable colloidal particles, which acted as centers of crystallization upon subsequent cooling.

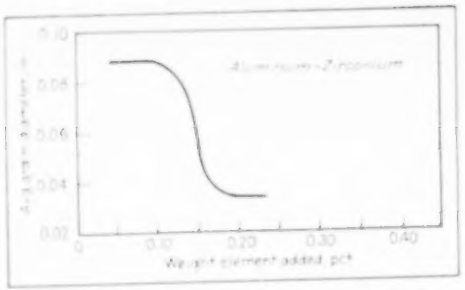


Fig. 4—The peritectic transformation may play a part in grain refinement in the cases of Zr, W, and Mo. The grain refinement curve for Al-Zr is shown here.

The work of Cibula in 1949 extended the identification of the nucleating particles, based on theoretical considerations and experimental data. He examined the active grain refiners and found that, with the exception of boron, all were transition elements. The elements likely to be present in molten aluminum or its environment, he reasoned, were oxygen, nitrogen, carbon, and hydrogen. With this as a basis, he proceeded to identify the compounds which acted as nucleating particles. The compounds had to satisfy two criteria: Stability in molten aluminum and similarity of lattice structure with aluminum. In the latter group of elements, only the carbides met these criteria satisfactorily.

Of the transition elements, only those which form interstitial carbides are active grain refiners. These carbides have high stability and are structurally compatible with aluminum. They have simple cubic or hexagonal structures and their atomic diameters are similar to that of aluminum. The transition elements which are nonrefiners form complex carbides with relatively low stability. For example, TiC has a cubic structure, simple formula, and high negative free energy of formation, about 55,000 cal per g atom. Fe_3C has a complex formula and structure, and a positive free energy of formation, 1000 cal per g atom. These structural requirements are equally applicable to the intermetallic compounds, and AlB_2 appears to meet them, while the transition element aluminides like $TiAl_3$ $MoAl_5$ do not. A summary of the characteristics of the active grain refiners is listed in Table II.

Cibula's experimental work included centrifuging small melts of aluminum-0.1 pct titanium alloy, which is normally fine grained. This produced a coarse grained solid, except for the base of the specimen, which indicated that the nuclei had segregated to the base. Particles in the base were examined by X-ray and identified as TiC.

Despite the lack of undercooling in aluminum melts to which active grain refiners had been added, he concluded that refinement was caused by both active nucleation and the restriction of crystal growth by concentration gradients set up by the grain refiner. While the total amount of grain refiner added appears small, it is a fact that grain refiners are more effective at low concentrations in the binary alloys than in elementary aluminum. Boron was reported by DePierre and Bernstein[15] as being more effective in the aluminum-5 pct silicon alloy than in elementary aluminum.

Table II. Characteristics of the Active Grain Refiners

	B	Cb	Mo	Ti	W	Zr
Melting point, °C	2300	2415	2625	1820	3410	1750
Max. solubility[a] at 720°C, pct	Low	0.00	0.36	0.15	0.16	0.22
Peritectic transformation	No	Yes	Yes	Yes	Yes	Yes
Threshold concentration	No	No	Yes	No	Yes	Yes
Compatible stable carbides	No	Yes	Yes	Yes	Yes	Yes
Compatible stable aluminides	Yes	No	No	No		No

Effect of Vibrations

It is known that the passage of vibrations of various frequencies through the melt influences solidification characteristics. While this influence has generally been exerted in the direction of refinement, in one instance coarsening was reported.[16] This was attributed to the leveling of the concentration gradients by the vibrations. The refining effect of vibrations was associated by Schmid and Ehret[17] with the elimination of undercooling in antimony melts, which indicates active nucleation. Schmid and Roll,[18] working with Wood's metal, theorized that the refining effect of vibrations was caused by frictional forces between the solidifying crystals and the liquid metal, indicating restriction of crystal growth. The effect of vibrations admittedly is a complex one.

There appear to be many mechanisms acting singly or in concert, which are capable of producing grain refinement. It is to be hoped that future work will help clarify the picture.

References

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[11] V. DePierre and H. Bernstein: Grain Refinement in Cast Aluminum. *Iron Age*, Vol. 163, No. 3, 20 January 1949.

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[13] Recorder II—Research Progress. *Metal Industry* Vol. 76, Apr. 14, 1950.

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Titanium Symposium to Highlight IMD Fall Meeting Program At Metal Congress

Sessions Will Be Held Oct. 20 to 22, 1952, at Adelphia Hotel, Philadelphia

THE technical program of the Institute of Metals Div., AIME, at the National Metal Congress and Exposition, Oct. 20 to 22, 1952, at Philadelphia, will feature an all day Titanium Symposium by world renowned experts in that field. The Research in Progress sessions, inaugurated in 1950 to bring to light research not far enough advanced to establish final results, have received a great deal of interest, and are being continued.

Headquarters of the IMD during the Metal Show will be the Adelphia Hotel, and all IMD technical sessions will be held there. Registration desks will be open on Sunday, October 19, from 3 to 9 pm, Monday from 8 am to 5 pm, Tuesday from 8 am to 5 pm, and Wednesday from 9 am to 4 pm. AIME member registration fee is $2, and for nonmembers, $4. No admission will be charged for AIME Student Associates, but other students will pay $1. Reprints of most of the papers will be presented to registrants.

The annual IMD Fall Dinner will be held at 7 pm Tuesday, October 21, in the Crystal Room of the Adelphia Hotel. Philadelphia Local Section, AIME, will provide a complimentary cocktail party for all dinner guests at 6 pm in the Jefferson Room of the hotel, immediately preceding the dinner. Dress will be informal (business suits).

SUNDAY, OCTOBER 19

8:00 pm, Junior Room

IMD Program Committee Meeting

MONDAY, OCTOBER 20

9:00 am to 12:00 m, Crystal Room

Thermodynamic and Thermal Properties

J. P. Nielsen, Chairman; D. J. Blackwede, Secretary

Scaling of Lead in Air: Elmer Weber, Chase Brass & Copper Co.; W. M. Baldwin, Jr., Case Institute of Technology. JOURNAL OF METALS, August 1952.

Concentration Dependence of Diffusion Coefficients in Metallic Solid Solutions: D. E. Thomas, Westinghouse Atomic Power Div.; C. E. Birchenall, Carnegie Institute of Technology. JOURNAL OF METALS, August 1952.

Thermodynamic Properties of Solid Nickel-Gold Alloys: L. L. Seigle, Sylvania Electric Products, Inc.; M. Cohen and B. L. Averbach, Massachusetts Institute of Technology.

Transformation in Cobalt-Nickel Alloys: J. B. Hess, Kaiser Aluminum & Chemical Corp.; C. S. Barrett, University of Chicago. JOURNAL OF METALS, June 1952.

Principles of Zone Melting: W. G. Pfann, Bell Telephone Laboratories. JOURNAL OF METALS, July 1952.

Segregation of Two Solutes, with Particular Reference to Semiconductors: W. G. Pfann, Bell Telephone Laboratories. JOURNAL OF METALS, August 1952.

9:00 am to 12:00 m, Jefferson Room

High Temperature

L. A. Carapella, Chairman; F. P. Bens, Secretary

Some Observations of Subgrain Formation During Creep in High Purity Aluminum: I. S. Servi, Union Carbide & Carbon Corp.; J. T. Norton and N. J. Grant, Massachusetts Institute of Technology. JOURNAL OF METALS, September 1952.

Observations of Creep of the Grain Boundary in High Purity Aluminum: H. C. Chang and N. J. Grant, Massachusetts Institute of Technology. JOURNAL OF METALS, June 1952.

Creep Correlations in Alpha Solid Solutions of Aluminum: O. D. Sherby and J. E. Dorn, University of California. JOURNAL OF METALS, September 1952.

Effect of Zirconium on Magnesium-Thorium and Magnesium-Thorium-Cerium Alloys: T. E. Leontis, Dow Chemical Co. JOURNAL OF METALS, June 1952.

Influence of Chemical Composition on the Rupture Properties at 1200°F of Wrought Cr-Ni-Co-Fe-Mo-W-Cb Alloys: E. E. Reynolds, Allegheny Ludlum Steel Corp.; J. W. Freeman and A. E. White, University of Michigan. JOURNAL OF METALS, September 1952.

High Temperature Oxidation of Some Iron Chromium Alloys: D. Caplan and M. Cohen, National Research Council, Ottawa.

Mechanical Properties of Intermetallic Compounds at Elevated Temperature: Robert Lowrie, Lewis Flight Propulsion Laboratory.

2:00 pm to 5:00 pm, Crystal Room

Research in Progress

(Abstracts of papers to be presented at this session will appear in the October issue of JOURNAL OF METALS)

4:30 pm, Junior Room

Membership Committee

6:30 pm, Coral Room

IMD Executive Committee Dinner Meeting

TUESDAY, OCTOBER 21

9:00 am to 12:00 m, Crystal Room

Symposium on Titanium and Titanium Alloys

M. A. Hunter and J. R. Long, Chairmen

Early History of Titanium: M. A. Hunter, Rensselaer Polytechnic Institute.

Developments Leading to Present Technology: J. R. Long, Minerals and Metals Advisory Board.

Significance of Titanium in Air Frame Construction: Col. J. S. Dick, Air Force Materiel Command.
Titanium as an Ordnance Material: Col. B. S. Mesick, Ordnance Corp., Watertown Arsenal.
Titanium as a Naval Material: E. L. Beardman, Office of Naval Materials.
New Processes for Reduction of Titanium: R. S. Dean, Consulting Engineer.
Dimensional Fabrication of Titanium Without Melting: G. S. Davies, Brush Development Co.

9:00 am to 12:00 m, Jefferson Room

Deformation

T. E. Leontis, Chairman, H. Y. Hunsicker, Secretary

Dynamic Formation of Slip Bands in Aluminum: N. K. Chen and R. B. Pond, Johns Hopkins University.
Observations on the Tension Texture of Aluminum: E. A. Calnan and Betty E. Williams, National Physical Laboratory. JOURNAL OF METALS, July 1952.
Information of Zinc Bicrystals by Thermal Ratcheting: J. E. Burke and Anna M. Turkalo, General Electric Co. JOURNAL OF METALS, June 1952.
Surface Effects in the Slip and Twinning of Metal Monocrystals: J. J. Gilman and T. A. Read, Columbia University. JOURNAL OF METALS, August 1952.
Kinking in Zinc Single Crystal Tension Specimens: Jack Washburn and E. R. Parker, University of California.

2:00 pm to 5:00 pm, Crystal Room

Symposium on Titanium and Titanium Alloys

M. A. Hunter and J. R. Long, Chairmen

Currently Available Alloys: Forgings and Bars: L. R. Frazier, General Electric Co.
Sheet and Strip:
Recent Metallurgical Developments:
Thomas Lippert, Titanium Metals Corp. of America.
W. L. Finlay, Rem-Cru Titanium, Inc.
F. H. Vandenburgh, Mallory-Sharon Titanium.
R. H. Whitmer, Republic Steel Corp.
E. H. Gee, E. I. duPont deNemours & Co., Inc.
Discussion.

2:00 pm to 5:00 pm, Jefferson Room

Physical Metallurgy

T. A. Read, Chairman, R. L. Fullman, Secretary

Development of Mechanical and Magnetic Hardness in a 10 Pct Vanadium-Cobalt-Iron Alloy: R. W. Fountain, Union Carbide & Carbon Corp.; J. F. Libsch, Lehigh University.
Observations on Nodular Graphites: H. M. Weld, R. L. Cunningham, and F. W. C. Boswell, Dept. of Mines & Technical Surveys. JOURNAL OF METALS, July 1952.
Strain Patterns in Charpy Impact Specimens of 0.20 Pct Carbon Mild Steel: R. S. Bumps, Studebaker Corp.
Recrystallization Kinetics of Low Carbon Steel: S. F. Reiter, General Electric Co. JOURNAL OF METALS, September 1952.
Effect of Molybdenum and of Nickel on the Rate of Nucleation and the Rate of Growth of Pearlite: R. W. Parcel, Rem-Cru Titanium, Inc.; R. F. Mehl, Carnegie Institute of Technology. JOURNAL OF METALS, July 1952.
Effect of Applied Stress on the Martensitic Transformation: S. A. Kulin, Westinghouse Atomic Power Div.; M. Cohen and B. L. Averbach, Massachusetts Institute of Technology. JOURNAL OF METALS, June 1952.
Study of Grain Shape in an Aluminum Alloy and Other Applications of Stereoscopic Macroradiography: W. M. Williams, Revere Copper & Brass Co.; C. S. Smith, University of Chicago. JOURNAL OF METALS, July 1952.

4:30 pm, Junior Room

IMD Publications Committee Meeting

6:00 pm, Jefferson Room

Cocktail party for IMD dinner guests. Courtesy Philadelphia Section, AIME.

7:00 pm, Crystal Room

IMD Dinner

WEDNESDAY, OCTOBER 22

12:15 pm, Coral Room

IMD Power Metal Committee Luncheon Meeting

2:00 pm to 5:00 pm, Crystal Room

Titanium

J. E. Burke, Chairman, E. S. Greiner, Secretary

Titanium-Chromium Phase Diagram: F. B. Cuff, N. J. Grant, and C. F. Floe, Massachusetts Institute of Technology. JOURNAL OF METALS, August 1952.
Titanium-Copper Binary Phase Diagram: A. Joukainen, E. I. duPont deNemours & Co., Inc.; N. J. Grant and C. F. Floe, Massachusetts Institute of Technology. JOURNAL OF METALS, July 1952.
Titanium-Aluminum Systems: E. S. Bumps, D. Kessler, and M. Hansen, Armour Research Foundation of Illinois Institute of Technology. JOURNAL OF METALS, June 1952.
Partial Titanium-Vanadium Phase Diagram: Paul Pietrokowsky and Pol Duwez, California Institute of Technology. JOURNAL OF METALS, June 1952.
Observations on the Lattice Parameters of the Alpha and TiO Phases in the Titanium-Oxygen System: W. Rostoker, Armour Research Foundation of Illinois Institute of Technology. JOURNAL OF METALS, September 1952.
Nature of the Line Markings in Titanium and Alpha Titanium Alloys: C. M. Craighead, G. A. Lenning, and R. I. Jaffee, Battelle Memorial Institute.
Time-Temperature-Transformation Characteristics of Titanium-Molybdenum Alloys: D. J. DeLazaro, M. Hansen, R. E. Riley, and W. Rostoker, Armour Research Foundation of Illinois Institute of Technology. JOURNAL OF METALS, March 1952.
Compression Texture of Iodide Titanium: D. N. Williams and D. S. Eppelsheimer, Missouri School of Mines and Metallurgy. JOURNAL OF METALS, June 1952.

2:00 pm to 5:00 pm, Jefferson Room

Constitutional Diagrams

B. H. Alexander, Chairman, E. J. Dotter, Secretary

Tungsten-Cobalt-Carbon System: Pekka Rautala and J. T. Norton, Massachusetts Institute of Technology.
Role of the Binder Phase in Cemented Tungsten-Carbide-Cobalt Alloys: Joseph Garland, Firth Sterling Steel & Carbide Corp.; J. T. Norton, Massachusetts Institute of Technology.
System Molybdenum Boron and Some Properties of the Molybdenum Borides: Robert Steinitz, Ira Binder, and David Moskowitz, American Electro Metal Corp. JOURNAL OF METALS, September 1952.
A Thermal and Dilatometric Investigation of the Alloys of Cobalt with Chromium and Molybdenum: A. G. Metcalfe, Deloro Smelting & Refining Co.
Systems Zirconium-Molybdenum and Zirconium-Wolfram: R. F. Domagala, D. J. McPherson, and M. Hansen, Armour Research Foundation of Illinois Institute of Technology.
Copper-Zinc Constitution Diagram Redetermined in the Vicinity of the Beta Phase by Means of Quantitative Metallography: Lilian Beck and C. S. Smith, University of Chicago.
Intermediate Phases in the Mo-Fe-Co, Mo-Fe-Ni, and Mo-Ni-Co Systems: D. K. Das, Notre Dame; S. P. Rideout, E. I. duPont deNemours Argonne National Laboratory; P. A. Beck, University of Illinois.

Use of Oxygen in the Bessemer Converter

by W. T. Rogers and L. T. Sanchez

This paper presents the results of a production experiment evaluating the effect of the use of oxygen in the bessemer converter with respect to its relation to blowing time, amount of steel scrap or cold pig iron which can be melted and teeming temperatures of the molten steel.

THE simplest and probably the most efficient and economical means for producing steel from molten pig iron is the bessemer converter. This process is essentially a mechanism for bringing oxygen into contact with the molten metal thereby oxidizing the elements silicon, manganese, and carbon. The source of oxygen is that contained in the air and is limited by that amount. In theory, there is an intermediate chemical reaction due to the mass action of iron and air which is represented by the equation:

$$2Fe + O_2 = 2FeO$$

The FeO then becomes the oxidizing agent and reacts with the silicon, manganese, and carbon to produce silicon dioxide (SiO_2), manganese oxide (MnO), and carbon monoxide (CO), in the order mentioned. The balancing of the various chemical reactions shows that in the ordinary bessemer process more than sufficient oxygen is delivered to satisfy these reactions, which indicates that a further increase in the oxygen content of the air would serve no useful purpose. In spite of this reasoning, however, it will be demonstrated that when melting steel scrap, commercially pure industrial oxygen introduced into the normal air blast will permit the melting of a larger proportion of steel scrap than is possible with air alone and also will increase the production rate by a substantial reduction in blowing time. It will also be shown that when melting cold pig iron, it is possible to melt up to twice as much pig iron with the use of oxygen as can be melted without added oxygen with a nominal increase in blowing time.

At the plant where this study was made, oxygen is purchased from a nearby supplier and piped directly into the plant. It is supplied to the bessemer converter by being introduced directly into the blast line through an automatic control system which may be adjusted by the bessemer operator or "blower." Normally, iron is supplied by five blast furnaces to an open hearth shop containing twelve 165-ton capacity stationary furnaces and a bessemer converting shop having three 30-ton converters. The molten metal from the blast furnaces is allocated to one shop or the other in a manner to best provide for maximum production. At various times, it is desirable to direct the maximum amount of available blast furnace production to the open hearth shop. This has the effect of reducing the production of the bessemer shop. When this condition exists, it is desirable to supplement the reduced iron charge at the bessemer with steel scrap or cold pig iron to the maximum possible extent in order to maintain high total ingot production. This condition becomes aggravated when one of the blast furnaces is taken out of production for any repair job and particularly for extended periods such as when relining is necessary.

The purpose of the investigation and experimentation with oxygen was to determine whether or not it would contribute to increased flexibility in the use of the raw materials, molten iron, steel scrap, and cold pig iron. In addition to the effect of oxygen on flexibility of operation, it was also necessary to determine the relation of its use to production rate or "blowing time," final finishing temperature of the steel or "teeming temperature," and steel quality.

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The objective then, is to evaluate the effects of the use of oxygen on the following factors: 1—maximum amount of steel scrap or cold pig iron which can be used to replace molten iron, 2—production rate or blowing time, 3—teeming temperature, 4—economy in the use of oxygen, and 5—effect on steel quality.

Procedure

After the equipment to supply oxygen to the air blast was installed, several blows of steel were made to familiarize the operating personnel with the use of the equipment. Following this, 145 blows

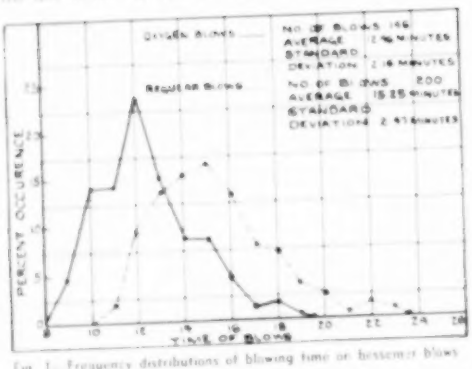

Fig. 1—Frequency distributions of blowing time on bessemer blows

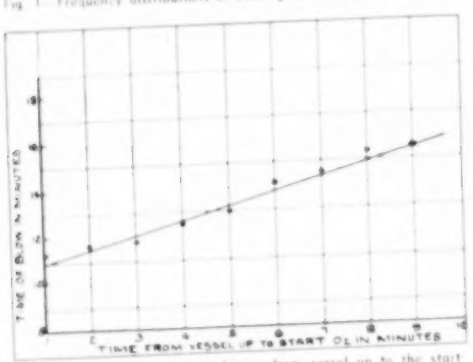

Fig. 2—Independent relation of time from vessel up to the start of oxygen to time of blow

using steel scrap were processed on which the following variables were studied with respect to their effect on blowing time and temperature within the ranges shown:

1—Time from vessel up to start oxygen, 1 to 9 min
2—Interval of time oxygen was used, 2 to 7 min
3—Rate of oxygen flow, 820 to 1520 cu ft per min
4—Total oxygen used, 1900 to 8400 cu ft
5—Number of blank tuyeres, 5 to 16
6—Scrap in total charge, 5.9 to 21.2 pct
7—Total charge weight, 64,000 to 73,500 lb
8—Silicon in iron, 0.95 to 1.85 pct

For purposes of comparison, during the same period, 200 blows were made using steel scrap without oxygen. Following this, an additional series of 144 blows was processed using various amounts of cold pig iron and oxygen-enriched blast; these blows were compared to a group of 279 blows made during the same period using cold pig iron and no oxygen.

The data on heats using steel scrap were analyzed by the use of multiple regression methods. Simple correlation coefficients were developed between each of the variables with blowing time and teeming temperature, following which a multiple regression equation was developed with those factors which were found to be significant. In this manner, it was possible to evaluate each related factor separately and secure the maximum efficiency in the use of data. The blows using cold pig iron were evaluated by summarizing in various increments of cold pig iron charged and comparing the results to estimates

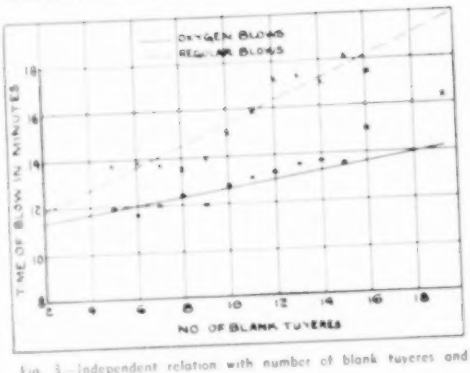

Fig. 3—Independent relation with number of blank tuyeres and time of blow

developed by the use of the regression equations for steel scrap blows.

Discussion

The main purpose of this report is to determine the value of introducing oxygen into the bessemer air blast with respect to its melting capabilities, and the effect of various amounts of steel scrap or cold pig iron and oxygen on production rate or blowing time. It is well known that the number of blank tuyeres in the vessel bottom and the silicon content of the blast furnace iron are two important factors affecting blowing time. It is therefore evident that the evaluation of the effect of oxygen on a production basis must be done by some method which will allow for the effects of variability in these related variables. The application of multiple regression analysis, and its faculty for giving a well-rounded evaluation in this particular type of problem, will be evident from the following discussion.

Use of Oxygen with Steel Scrap

There is a distinct difference in the behavior of steel scrap and that of cold pig iron. It is pointed out at this time that conclusions with respect to one cannot be applied to the other. The discussion will therefore have two subdivisions: one devoted to the use of steel scrap, and the other to the use of cold pig iron. In Fig. 1, frequency distributions directly comparing steel scrap blows using oxygen with regular blows are presented. From these curves, it is evident that the use of oxygen reduces the blowing time on the average by 2.79 min. It is also shown that blows using oxygen have a much more consistent distribution of blowing times, since the mode of the oxygen blows represents 23 pct of the total and has a range of 9 to 19 min, whereas, the mode of the regular blows represents only 17 pct of the distribution and has a range of 11 to 23 min.

The standard deviation of oxygen blows is 2.16 min as compared to 2.47 min on regular blows.

Frequency distributions, while giving an overall comparison, do not furnish sufficient information to properly determine the real difference which would exist if similar variables were held constant in both distributions. In order to evaluate more accurately the actual difference which exists under similar conditions and put the comparative results on a common basis, a multiple regression equation is developed for each group of heats. These equations include those factors which are common to and effective in determining the variability of the blowing time. The equations for those variables which were found related to blowing time are as follows:

1—Blows with Oxygen: blowing time = 8.14 + 0.5746 × time from vessel up to start oxygen + 0.1611 × number of blank tuyeres + 3.3000 × percent silicon in blast furnace iron − 0.2770 × percent scrap in the total charge.

2—Regular Blows: blowing time = 5.44 + 0.4536 × number of blank tuyeres + 3.180 × percent silicon in blast furnace iron + 0.0320 × percent scrap in the total charge.

The independent relation developed for each of the factors included in the above equations is shown graphically in Figs. 2 to 5 with the following discussion bringing out the pertinent facts portrayed by each illustration.

Effect of Oxygen on Blowing Time: In the multiple regression analysis, four factors relating to the use of oxygen were evaluated: 1—the time from turning the vessel up until the use of oxygen was started, 2—the rate of flow of oxygen (cu ft per min), 3—the elapsed time during which oxygen was used, and 4—the total amount of oxygen consumed.

Only one of these variables, time from vessel up to start oxygen, gave sufficient evidence of relationship to be considered significant. The effect of this factor on blowing time is presented in Fig. 2, which shows that a straight line relationship exists and blowing time increases 0.57 min for each increase of 1 min in the time from vessel up to start oxygen. Conclusions made from this evaluation are that, within the range of the variables studied, the amount of oxygen, the rate of flow, and the length of time it is used are not important with respect to variability of blowing time. The one important factor is the elapsed time from turning the vessel up until the oxygen is introduced into the air blast. However, the use of oxygen too soon after the start of the blow, while reducing the blowing time, is not conducive to the maximum steel scrap melting, which is the important consideration under present operating conditions. The most efficient scrap melting practice has been obtained by introducing the oxygen into the blast coincident with the start of the carbon flame. In connection with the factor length of time oxygen is used, although the actual range of data shows 2 to 7 min, practically all of the observations were of 4 and 5 min periods. In view of this fact, the statement with respect to length of time oxygen is used should be that no difference is observed in this range.

Effect of Blank Tuyeres on Blowing Time: The bessemer converter bottom on the vessels used in this study has 31 tuyeres, of which 5 are preblanked, leaving a maximum of 26 open tuyeres available for blowing. Since the tuyeres introduce the air blast into the bessemer charge, it is evident that the efficiency of the process decreases as the number of open tuyeres is reduced. The effect of taking tuyeres out of service, or "blanking," is shown graphically in Fig. 3 for both oxygenated and regular blows. Referring to the previous equations, it will be noted that blowing time increases 0.16 min for each additional blank tuyere when oxygen is used and 0.45 min with no oxygen. In comparing the two trend lines in Fig. 3, it will be noted that with 5 blank tuyeres or at the start of the vessel bottom life, the oxygen blows show a reduction of 1.4 min over the regular blows. At 10 blanks, this difference increases to 2.7 min, and with 16 blanks, it becomes 4.7 min.

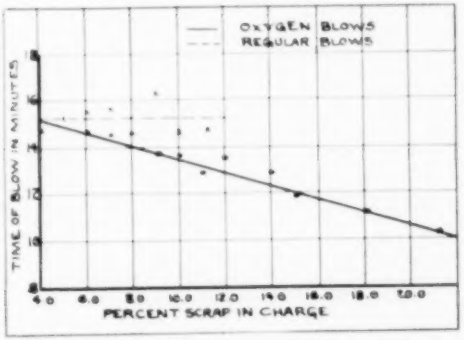

Fig. 4—Independent relation of percentage of scrap in charge to time of blow.

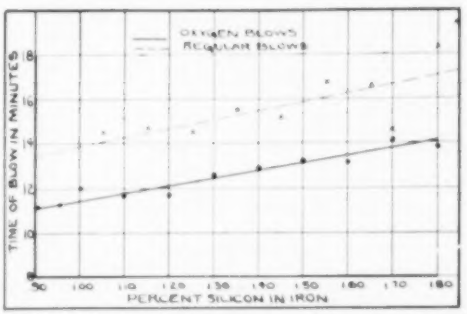

Fig. 5—Independent relation of percentage of silicon in iron to time of blow.

It is of further interest that Fig. 3 indicates that the use of oxygen has the potentiality of increasing the service which can be obtained from a vessel bottom without affecting the blowing time too adversely. From the configuration of the actual points on the regular blows, it is shown that no increase in blowing time is obtained until 10 tuyeres are blanked, and, thereafter, it increases approximately 1 min for each additional blank tuyere. There is only slight evidence of the same type of relation on oxygenated blows. For purposes of practical application, the use of oxygen may be employed as a means of increasing the bottom life through the use of oxygen after 9 tuyeres are blanked and continuing its use throughout the remainder of the bottom life or until 16 to 20 tuyeres have been blanked.

Effect of Steel Scrap in the Charge on Blowing Time: The main interest in connection with the use of oxygen is its effect on the amount of steel scrap

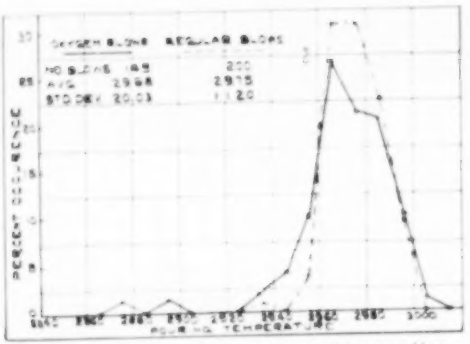

Fig. 6—Frequency distributions of temperature of bessemer blows.

which can be melted. Every additional ton of steel scrap which can be melted in the bessemer makes an additional ton of molten pig iron available to the plant, and, consequently, maintains the maximum bessemer ingot production.

The effect of steel scrap charged on blowing time is presented in Fig. 4 for both oxygen and regular blows. The range of scrap charged on regular blows is from 4 to 12 pct and there is no evidence of relationship with time of blow in this range. On the oxygenated blows with a scrap range from 3.9 to 21.2 pct, it is shown that time of blow is reduced 0.28 min for each 1 pct increase in scrap charged. In general, the determination of the amount of scrap to be charged was based on the amount of silicon in the iron.

Effect of Silicon in Blast Furnace Iron on Blowing Time. Silicon is the one element to be eliminated from the blast furnace iron which presented the greatest variability with values ranging from 0.93 to 1.85 pct. The effect of this element on blowing time for both regular and oxygenated blows is presented in Fig. 5, which shows that there is approximately the same relation in both cases with the time of blow increasing 3.3 min for each 1.0 pct Si on regular blows and 3.8 min for each 1 pct on oxygen blows. In consideration of the data presented in Figs. 4 and 5, it is evident that the proportion of steel scrap charged should be increased materially on high silicon oxygen blows in order to reduce the time of blow and get the most satisfactory results from various combinations of these two factors when oxygen is being used. However, ensuing discussion of teeming temperatures will show that scrap usage is limited because of temperature considerations.

Effect of Oxygen on Temperature of Finished Steel. While the blowing time and amount of steel scrap which can be melted are important considerations, another factor of major importance is the teeming temperature of the steel. Frequency distributions of pouring temperature comparing oxygen and regular blows are presented in Fig. 6. It is evident from this comparison that the difference in average teeming temperature of 2968 F on oxygen blows and 2975 F on regular is not sufficiently large to be considered significant. The standard deviations, however, show a real difference in variability with the oxygen blows having a greater temperature range than the regular blows. This difference is attributed to lack of extended experience with the use of oxygen and not to any factor introduced into the process by the use of oxygen. It can be expected that with increased experience the proportion of cold blows which are mainly responsible for the increased variability will be eliminated.

Table I Blowing Time and Pouring Temperature for Various Levels of Steel Scrap and Silicon

Scrap		Silicon, Pct		
		0.90–1.19	1.20–1.49	1.50–1.90
Lb	Pct	Blowing Time (Min) and Temperature (F)		
2,000	3.9	14.3 2972 2943–3001	15.6 2978 2956–3000	16.7 2980 2958–3017
4,000	8.0	13.4 2967 2938–2996	14.9 2971 2946–2994	15.9 2981 2954–3012
6,000	11.9	12.6 2962 2933–2991	14.0 2970 2941–2999	15.0 2979 2950–3008
8,000	15.9	11.8 2957 2928–2986	13.1 2966 2937–2995	14.1 2974 2945–3003
10,000	19.9	10.9 2953 2924–2982	12.4 2961 2932–2990	13.4 2968 2940–2996
12,000	23.9	10.1 2948 2919–2977	11.5 2956 2927–2985	12.5 2963 2934–2992

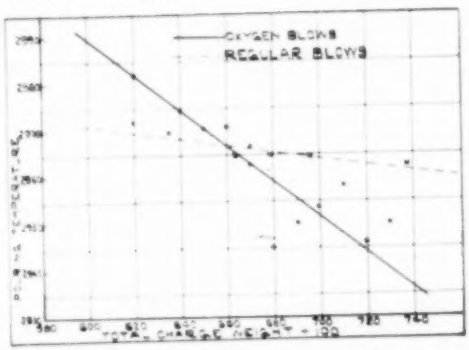

Fig. 7—Independent relation of total charge weight to pouring temperature.

In the analysis of factors associated with teeming temperature, it is of interest that the use of oxygen is in no way associated with final temperature. This is in line with the theory that the total heat produced is dependent on the composition of the iron rather than on the increased amount of oxygen in the blast. The final results of the multiple regression analysis show that three factors are related to temperature on both oxygen and regular blows: 1—total charge weight, 2—percent scrap charged, and 3—percent silicon in iron. The equations representing the effect of these factors are:

1—With Oxygen: pouring temperature = 2969 − 0.0003 × total charge weight − 1.57 × percent scrap charged + 26.20 × percent silicon in blast furnace iron.

2—Without Oxygen: pouring temperature = 3222 − 0.0038 × total charge weight − 1.78 × percent scrap charged + 17.00 × percent silicon in blast furnace iron.

The individual independent relations with these factors are presented in Figs. 7 to 9.

Effect of Total Charge Weight on Pouring Temperature. The effect of variation in total charge weight on pouring temperature is shown in Fig. 7. The calculated regression lines on this graph indicate an inverse relationship on both oxygenated and regular blows. It will be noted from this representation of data that the effect of charge weight is much more pronounced on oxygen blows than on regular blows. The reason for this relation is not fully comprehended, but there is no doubt of its existence from the evidence presented.

Effect of Steel Scrap on Pouring Temperature. The addition of steel scrap to the converter charge has long been known, it is used as a standard operating practice in many plants to control the temperature of regular bessemer blows. The graphic presentation of its actual effect in reducing temperature on both regular and oxygen blows is exhibited in Fig. 8. It is shown by these curves and also by the previous equations that final pouring temperature is reduced at approximately the same rate in both cases. These relations are in line with generally accepted theory and serve to bear out the knowledge gained by the

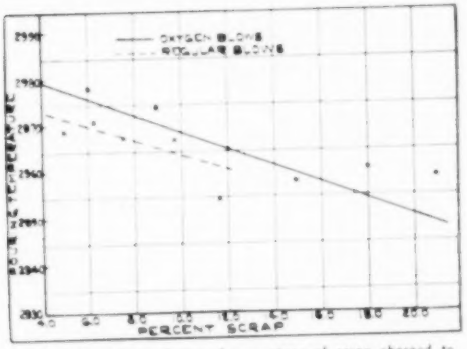

Fig. 8—Independent relation of percentage of scrap charged to pouring temperature.

operators that steel scrap is a good means of controlling excessive temperatures.

Effect of Silicon in Blast Furnace Iron on Pouring Temperatures: Just as steel scrap works to reduce the pouring temperature, silicon in the blast furnace iron operates to increase it. The relations with silicon are presented in Fig. 9 where it is evident that silicon exerts a more pronounced effect on the temperature of regular blows than it does on oxygen blows.

Practical Application of the Multiple Correlation Study on Heats Using Steel Scrap: Under operating conditions of iron shortage, the main interest in the use of oxygen centers around its effect on the amount of additional scrap which can be melted in a bessemer converter. From the foregoing analysis, it has been shown that increased amounts of scrap shorten the blowing time and reduce the final pouring temperature on oxygenated blows. It has also been demonstrated that silicon in the blast furnace iron increases the blowing time and the pouring temperature. On the basis of the opposing effects of these two variables, one of which, the steel scrap, is subject to positive control, and the other, the silicon, which must be handled as it is received, it is possible to set up an estimating table which will

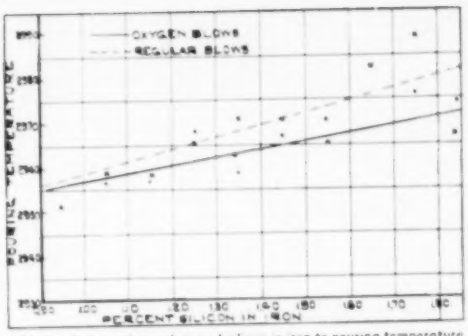

Fig. 9—Independent relation of silicon in iron to pouring temperature.

show for various increments of scrap and specified ranges of silicon, the blowing time and pouring temperature that can be expected. This tabulation is presented in Table I. It will be noted that in addition to the average pouring temperature, an expected range of temperature is shown. This range is calculated on the basis of 2.6 σ limits of expectancy from the standard deviation obtained on regular blows, since with added experience the operators will attain at least this much control. With this limit, it can be expected that only one blow in 200 will be outside the range shown.

From Table I, a standard practice for the use of oxygen was developed from three levels of silicon using an amount of steel scrap which would insure the average observed temperature to be in the range of 2960° to 2965 F, a level which is believed to be as low as possible consistent with good pouring practice and satisfactory steel quality. This standard practice is presented in Table II which also includes the average conditions on regular blows for comparative purposes and shows the additional steel scrap which can be melted for various levels of silicon in blast furnace iron.

From this standard practice tabulation, it is evident that when it is desirable to melt as much steel scrap as possible, it is also desirable to have high silicon blast furnace iron. This condition will also contribute to improved steel quality, as higher silicon is usually associated with the low sulphur content of the iron. A higher silicon-manganese ratio will also be obtained and tend to enhance the quality of the steel as well as produce good blowing operations. With the use of oxygen, an additional 2000 to

Table II Standard Practice for the Use of Oxygen

Silicon in hot metal	1.40	0.90–1.19	1.20–1.49	1.50–1.90
	Regular Blows	Oxygenated Blows		
Steel, lb	4,000	6,000	9,000	12,000
Hot metal, lb	63,000	61,000	58,000	55,000
Total charge, lb	67,000	67,000	67,000	67,000
Total time of blow, min	15.3	12.6	12.7	12.5
		Start of carbon flame		
Time start oxygen into blast		1,000		1,000
Rate of flow of O_2, cu ft per min		4	4	4
Oxygen used, min		4,000	4,000	4,000
O_2 consumed, cu ft				
Average total blast volume, cu ft	480,000	371,000	373,000	368,000
O_2 in total blast, pct	21.0	21.9	21.8	21.9
Scrap in charge, pct	6.0	9.0	13.4	17.9
Additional pounds of scrap per thousand cu ft O_2		500	1,200	2,000
Total additional scrap		2,000	4,800	8,000

Table III. Comparison of Regular Blows and Oxygen Blows Using Cold Pig Iron

	No. Heats	Cold Pig Charged, Lb: Average	Cold Pig Charged, Lb: Range	Vessel Up to start O, Min	O, Cu Ft per Min	O, Total Cu Ft	Average Cold Pig Iron, Pct	Average No. of Blanks	Average Si in Iron, Pct	Time of Blow: Actual	Time of Blow: Estimate	Time of Blow: Difference	Pouring Temperature, °F
Regular blows	279	4,880					7.4	8.9	1.33	15.9	14.0	1.9	2974
Oxygen blows	30	9,400	9,000 to 10,000	4.0	965	3870	14.0	7.9	1.17	14.5	11.9	2.6	2976
Oxygen blows	80	10,400	10,000 to 11,000	5.0	974	5065	15.5	6.4	1.46	17.7	13.3	4.4	2973
Oxygen blows	40	12,400	12,000 and over	6.0	970	5871	16.3	9.0	1.00	16.3	13.3	3.0	2978

8000 lb of steel scrap can be melted with a reduction of 2.6 min in blowing time over average conditions without oxygen for each silicon range.

Effect of Oxygen in Melting Cold Pig Iron

In evaluating the effect of oxygen on blows using cold pig iron, 144 blows using oxygen with various amounts of cold pig iron ranging from 8500 to 13,000 lb were compared to the results obtained on 279 regular blows with an average of 4880 lb of cold pig iron. The estimating equations for blows using steel scrap were applied to the pig iron blows thus permitting a direct comparison of blowing times between cold pig iron and steel scrap. The results of this comparison are presented in Table III. It is evident from this comparison that the substitution of pig iron results in a longer blowing time for any given amount of pig iron. This table also shows that the shortest blowing time is obtained with the use of oxygen and approximately 9500 lb of pig iron, but on further examination, it is seen that this condition would be expected from the average values exhibited for time from vessel up to start oxygen, number of blank tuyeres, and silicon in iron. It is obvious that to secure a reliable comparison, variations in these values should be adjusted to a common level. This can be done by applying the equations previously calculated for steel scrap. The result of this application brings out the following facts:

1—The use of cold pig iron in place of steel scrap on regular blows results in an increase of 1.9 min per blow.

2—With the use of oxygen, the amount of cold pig iron in the charge can be doubled and for similar conditions of other factors, the blowing time will increase only 0.7 min.

3—Cold pig iron in excess of 10,000 lb progressively increases blowing time to the extent that it is not recommended as a desirable practice from that viewpoint.

4—Pouring temperature is not materially affected with the use of cold pig iron.

Effect of Oxygen on Vessel Lining and Bottom Life. Observations throughout the conducting of the experiments with oxygen show that neither the vessel lining nor the bottom life was affected by its use.

Effect of Oxygen on Steel Quality. Steel quality is a major consideration in evaluating the effect of any change in practice. However, there are no indications that oxygen in the bessemer affects either the processing quality at the bessemer or steel quality at any subsequent processing point. Analysis of vessel slag, ladle slag, and nitrogen in the steel shows the slag on oxygen blows to be somewhat higher in FeO but indicates no difference in nitrogen content.

Comparative analysis of slag FeO and nitrogen are given in Table IV.

Table IV. Comparative Analysis of Slag FeO and Nitrogen

	FeO in Slag, Pct: Vessel	FeO in Slag, Pct: Ladle	Nitrogen in Steel, Pct
Regular Blows	18.06	12.66	0.0185
Oxygen Blows	20.49	16.83	0.0175

Conclusions

The result of the experience gained in the running of the experiments with the use of oxygen in the bessemer blast has been to establish a standard practice with respect to its effects which will permit the melting of considerably more steel scrap than can be melted without its use. It also can be of assistance in providing a greater flexibility in the use of steel scrap and molten pig iron so that a more efficient balance between the distribution of these two materials can be effected between the open hearth and bessemer shops. In addition, it has been shown that oxygen may be used to maintain a more uniform production rate by coupling the incidence of its use with the blanking of tuyeres and thus continue the productive rate of the converter throughout the normal span of bottom life instead of having it fall off after a nominal number of tuyeres are blanked.

It has also been determined that with the use of oxygen, a greater proportion of cold pig iron can be charged into the vessels than can normally be charged. However, the melting of cold pig iron increases the blowing time especially when its proportions exceed 14 pct, so that the most economical amount from a standpoint of productive capacity is 14 pct or less.

Evaluations of the effect of oxygen on final teeming temperatures indicate no difference from regular heats. The use of oxygen does not appear to affect vessel bottom life or final steel quality.

Acknowledgment

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Effect of Manganese on the Activity of Sulphur In Liquid Iron and Iron-Carbon Alloys

by J. P. Morris

PREVIOUS investigations[1] have shown that alloying elements in liquid iron influence the thermodynamic activity of sulphur and thereby affect the partition of sulphur between metal and slag in the desulphurization process. For example, the greater efficiency of desulphurization in the blast furnace as compared to the open hearth can be attributed in part to a higher level of sulphur activity in blast-furnace metal due to the higher concentration of carbon and silicon. In the present investigation, a short study was made of the influence of manganese on the activity of sulphur in liquid iron and iron-carbon alloys. In contrast to carbon and silicon, manganese was found to decrease the activity coefficient of sulphur; and in iron-carbon alloys it counteracts to some extent the influence of carbon. However, at manganese concentrations normally present in the blast furnace or open hearth, the effect of manganese is small.

Since manganese sulphide has a limited solubility in iron, manganese can act under certain conditions as a desulphurizing agent. Considerable data on the manganese-sulphur product in carbon-saturated melts were obtained in the investigation and have been included in this report.

The experimental procedure was the same as that used in the earlier investigations on the effect of silicon[2] and carbon[3] on sulphur activity. Briefly, the method was as follows: The molten alloy, contained in a graphite or sintered alumina crucible, was brought to equilibrium at a constant temperature with a mixture of hydrogen and hydrogen sulphide of constant composition by bubbling the gas through the metal. Samples of the melt were taken for analysis at regular intervals by suction through a 2 to 3 mm bore silica tube dipped into the metal. The experiments were run in a graphite spiral resistance furnace with melts weighing 50 to 60 g. The gas bubbling tubes were made of sintered alumina and were 5/16 in. OD, 1/16 in. ID, and 24 in. long. Equilibrium was assumed to have been attained when the sulphur content of the liquid metal reached a constant value.

During an experiment there was a rapid loss of manganese from the melt by volatilization. To offset this loss, small additions of manganese were made periodically. The rate of manganese addition needed to maintain a constant manganese concentration was determined in preliminary tests.

In all of the experiments, deposits of manganese sulphide formed above the melts in a cooler region of the furnace. Apparently, these deposits resulted from a reaction between manganese vapor and hydrogen sulphide in the gas. To prove that manganese sulphide did not volatilize from the melts to a measurable extent, an experiment was run in which helium was bubbled through liquid iron containing both manganese and sulphur. Although manganese volatilized rapidly in this test, there was no appreciable loss of sulphur. Volatilization of manganese sulphide from a melt would have led to an apparent equilibrium condition in which the sulphur content of the metal was lower than the true equilibrium value.

The experimental results are shown in the first seven columns of Table I. The data in the last two columns were obtained from the previous work on the effect of carbon[3] and show what the results would have been in the absence of manganese but with temperature, gas composition, and carbon content of the metal remaining the same. Comparison of the last four columns show that, in the presence of manganese, the sulphur content of the metal increased at equilibrium and the activity coefficient of sulphur decreased. However, the results show that, for manganese concentrations below 3 pct, the effect of manganese is small.

The values for activity coefficient of sulphur given in Table I were calculated from the following relations:

$$S \text{ (in liquid metal)} + H_2 \text{ (gas)} = H_2S \text{ (gas)} \quad [1]$$

$$K_{1600^\circ C} = \frac{p_{H_2S}}{\gamma_S \times \%S \times p_{H_2}} = 0.00251 \quad [2]$$

where K is the equilibrium constant for the reaction, p_{H_2S} and p_{H_2} are the partial pressures of hydrogen sulphide and hydrogen, respectively, and γ_S is the activity coefficient of sulphur. The standard state for sulphur was taken to be a 1 pct solution of sulphur in pure iron. The numerical value for K at 1600° C was determined in the earlier work.

For the purpose of showing graphically the results of the tests run at 1600° C, the activity coefficients of sulphur were recalculated so as to correspond to a manganese concentration in the metal of 2 pct in each case. In the calculation it was assumed that the increase in sulphur content of the metal at equilibrium caused by the presence of manganese

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Table I. Experimental Results and Comparison with Data for Manganese-free Metal

Expt. No.	Temperature, °C	$\frac{R \times}{R}$ x10⁻⁵	Carbon, Pct	Mn, Pct	Sulphur at Equilibrium, Pct	Activity Coefficient of Sulphur	Data on Mn-free Metal: Sulphur at Equilibrium, Pct	Data on Mn-free Metal: Activity Coefficient of Sulphur
124	1600	2.46	0.8	2.6	1.04	0.96	0.94	1.06
126	1600	2.46	2.2	1.9	0.54	1.77	0.49	1.96
127	1600	2.42	4.6	2.8	0.29	3.32	0.26	3.71
130	1600	2.42	4.6	2.8	0.17	5.65	0.145	6.31
125	1600	2.37	Saturated	2.6	0.18		0.17	
124	1500	2.40	Saturated	2.4	0.18		0.17	
105	1400	2.34	Saturated	1.0	0.29		0.19	

was directly proportional to the manganese concentration. The results are plotted in Fig. 1, with the results obtained previously for carbon and silicon.

Effect of Manganese on the Solubility Limit of Sulphur in Melts Saturated with Carbon

During several preliminary experiments on sulphur activity, a sulphide slag formed, indicating that the solubility limit of sulphur in the metal had been reached. To supplement the data on the solubility limit of sulphur obtained in these tests, two additional procedures were used: 1—Addition of manganese, stepwise, to a melt containing sulphur at a constant temperature, and 2—stepwise cooling of a melt containing both manganese and sulphur. The melts were made in graphite crucibles and stirred with helium bubbled into the metal through a graphite tube. Enough time was allowed in each step for attaining equilibrium before sampling. The amount of slag formed in an experiment was small, and slag samples of adequate size for analysis could not be obtained.

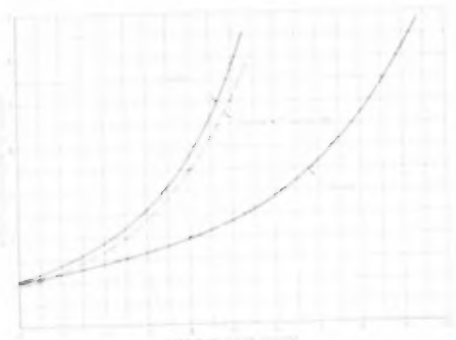

Fig. 1—Effect of carbon, carbon plus 2 pct manganese, and silicon on the activity coefficient of sulphur in iron at 1600°C.

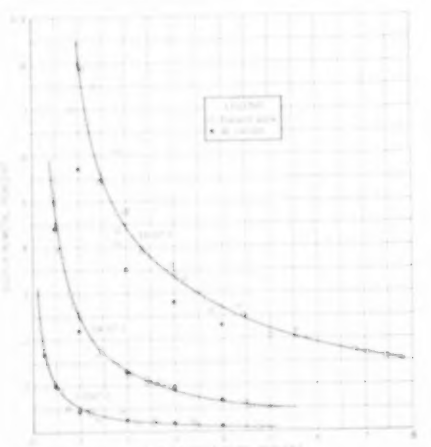

Fig. 2—Effect of manganese on the sulphur content of carbon saturated melts of iron in equilibrium with MnS-FeS slag.

The results of these experiments are shown in Fig. 2, together with the results of similar work by Oelsen.[3] The discrepancy between the two sets of data at 1600°C may have been due to errors in temperature measurement or to improper sampling in one or both investigations.

The reaction between manganese and sulphur in the metal and the value of the manganese-sulphur product can be represented by the following equations:

$$Mn + S = (MnS) \qquad [3]$$

$$\%Mn \times \%S = \frac{a_{MnS}}{K \times \gamma_{Mn} \times \gamma_S} \qquad [4]$$

where K is the equilibrium constant of the reaction, a_{MnS} is the activity of manganese sulphide in the slag, and γ_{Mn} and γ_S are the activity coefficients of manganese and sulphur in the metal, respectively.

The manganese-sulphur product in iron is not a true solubility product, since the slag phase contains FeS as well as MnS. Eq 4 shows that the value of the product depends upon the activity of MnS in the slag and upon the activity coefficients of manganese and sulphur in the metal. At 1200° and 1400°C, the present work shows that the products are nearly constant over the concentration range studied, the average values being about 0.05 and 0.26, respectively. At 1600°C, the product increases from 0.8 at 1 pct Mn to 1.2 at 7 pct Mn.

The curves in Fig. 2 give the maximum sulphur concentration that is possible in metal of a given manganese content and show that manganese alone is not an efficient desulphurizer, except at temperatures below the normal operating range. However, in the presence of an oxide slag, manganese may be more effective as a desulphurizer than is indicated in Fig. 2, since the activity of manganese sulphide in the slag would probably be much lower than in the pure sulphide slags formed in the present work.

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Heats of Solution of Group IB Metals in Liquid Tin

By L. B. Ticknor and M. B. Bever

An isothermal calorimeter suitable for measurements of heats of solution in liquid tin as solvent is described. Measurements of the heats of solution of gold, silver, copper, and a gold-silver alloy are reported. The heat of formation of this gold-silver alloy is also reported.

HEATS of solution in liquids can be determined directly, but few such data have been published for metals as solvents. Knowledge of heats of solution is desirable because it contributes to the general understanding of energy relations in metallic solutions. Thermochemical measurements of this type also furnish answers to specific problems: For example, from the heats of solution of an alloy and of a mixture of its constituent elements in a given solvent, the heat of formation of the alloy may be found. Similarly, differences in the energy content of samples of the same metal in two different states, such as the annealed and cold worked states, may be determined.

In the work reported here, gold, silver, and an alloy of gold and silver were dissolved in liquid tin at 240° C and gold, silver, and copper were dissolved in tin at 300° C. The experiments yielded the heats of solution of these metals in tin. The heat of formation of the gold-silver alloy was also determined. The same calorimetric method is being used to measure the energy stored in metals during cold working and preliminary results have been published.[1]

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Equipment and Experimental Procedure

The isothermal calorimeter used in this work, Fig. 1, consisted of a Dewar flask completely immersed in a constant-temperature salt bath. A long neck provided space for thermocouple leads and a stirrer shaft and permitted the injection of solute samples. The metal bath in the calorimeter flask was stirred at about 100 rpm by a small glass impeller driven by a constant-speed motor. The shaft of the stirrer passed through a Wilson vacuum seal.[2]

All measurements were made under vacuum in order to eliminate temperature disturbances resulting from gas convection and to prevent the oxidation of tin. The calorimeter flask was joined by an all-glass connecting line to a gas-control system which made possible the use of a protective atmosphere of deoxidized and dried hydrogen. At the operating temperature of the calorimeter tin oxide was not reduced by hydrogen, presumably because the reaction rate was too slow. Part of the closed system was a removable side tube through which the solute sample could be introduced and in which it was held at a temperature of 0° C prior to injection into the metal bath.

The salt bath containing a mixture of sodium, lithium, and potassium nitrates was similar to that described by Beattie[3] and was equipped with a stir-

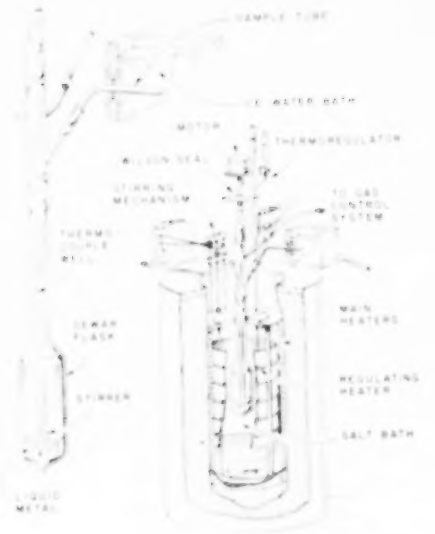

Fig. 1—View of calorimetric equipment

ring mechanism described by Collins.[7] The temperature was regulated by a mercury thermoregulator. The calorimeter could be operated at temperatures from 150° to approximately 320° C and with a different temperature control device the range could have been extended to 500° C.

A multiple iron-constantan thermocouple consisting of two pairs of junctions in series was used for measuring the metal bath temperature; the hot junctions were wound in the form of a close helix in order to reduce heat losses by conduction through the leads. The temperature of the salt bath was followed with a similar multiple thermocouple. The thermocouples were calibrated at the steam, mercury, and sulphur points. The electromotive forces were read on a potentiometer-galvanometer combination to 1 microvolt corresponding to a temperature difference of 0.01° C. Under steady conditions the temperature variation in the salt bath was about ±0.02° C and in the liquid metal less than ±0.01° C.

The tin contained metallic impurities totaling less than 0.003 pct according to the J. T. Baker Chemical Co. analysis. The purity of the gold was about 99.95 pct, that of the silver about 99.92 pct, and that of the gold-silver alloy 74.95 pct Au and 25.01 pct Ag according to the analyses of Handy & Harman. The copper was made by the process of Smart, Smith, and Phillips and the impurity limits stated by them applied to it. All solute metals were obtained in the form of wire of 0.032 in. diam. They were cleaned, cold-rolled into thin ribbon to increase the rate of solution, and annealed above their recrystallization ranges. The copper was deoxidized with hydrogen in the sample tube prior to injection into the metal bath. The tungsten wire used in the calibration had a diameter of 0.025 in.

In preparing a run tin metal stock was scraped to remove any oxide and was placed in the calorimeter flask. The flask was inserted into the salt bath and connected to the gas-control system. The air was pumped out and replaced with hydrogen; after changing the hydrogen several times a vacuum was established. Little oxidation took place in the short time required for these initial operations, during which the tin was at a low temperature because the heat transfer was slow. After the tin was melted, which required more than 4 hr, the metal bath stirrer was started. A sample of solute metal was placed in the sample tube, which was cooled in an ice-water bath.

About 4 hr after melting, the temperature of the liquid metal attained a steady state. The sample tube was then rotated about its ground glass joint into a vertical position and the solute metal dropped into the liquid metal in the calorimeter flask. The addition resulted in a change of the temperature of the liquid metal, which was followed at frequent intervals. The solute sample came to the temperature of the metal bath in about one-fourth of a minute as shown by the calibrating addition of tungsten and dissolved in 1 to 4 min with a few exceptions discussed later. About 5 to 10 min were required in most runs for the cooling or heating of the metal bath to become nearly exponential and about 1 hr elapsed before the bath returned to within 0.01° C of its original steady-state temperature.

In a typical run four successive additions were made. The heat capacity of the calorimeter was determined for each run from a fifth addition consisting of tungsten wire.

Method of Calculation

The method of evaluating calorimetric measurements as well as the design and operation of calorimeters are the subject of several treatises.[7,8] An outline of the methods of calculation used in the work reported here is nevertheless warranted.

Upon the addition of a sample of solute metal, the temperature of the metal bath first decreases slightly as the sample absorbs heat, and then decreases further or increases, depending on whether the dissolution process is endothermic or exothermic. The resulting difference in the temperatures of the metal bath and the salt bath causes an exchange of heat, which reduces the temperature change of the metal below the maximum which would be attained under adiabatic conditions. Eventually, the temperature of the metal bath returns to its original value by continued heat exchange with the surroundings, which consist mainly of the salt bath. During this later period, or "rating period," the exchange of heat can be followed quantitatively and the resulting measurements are used to calculate the heat exchanged during the period immediately after the addition, or "experimental period."[7]

The calculation of the total heat effect of a sample addition consists of two parts: 1—The temperature change at a certain time after adding the sample is multiplied by the heat capacity of the calorimeter, and 2—to this is added the heat exchanged with the surroundings during the interval.

For the first part of the calculation the heat capacity of the calorimeter, also known as its "water value," or "energy equivalent," is obtained from the calibration with tungsten wire and the published specific heat of tungsten.[9] The temperature change is taken for a time, t', at which the solution process is complete and nearly exponential cooling has begun as explained later. This time is taken as 10 min for all additions (except the fourth addition in run No. 2

for which 15 min had to be taken because of slow dissolution). The maximum observed temperature change varied from −5° to +2°C depending on the nature and quantity of solute added.

For the second part of the calculation, the rate of heat transfer is found by assuming Newton's law of exponential cooling. For small changes in temperature, a linear relation between the temperature and the electromotive force of the measuring thermocouple may be assumed. Newton's law can then be expressed by the equation:

$$\frac{d\Delta(\text{emf})}{dt} = -k\Delta(\text{emf}) \qquad [1a]$$

which upon integration yields:

$$\ln\Delta(\text{emf}) = -kt + \text{constant} \qquad [1b]$$

Δ(emf) is the difference of the instantaneous value of the electromotive force and the steady-state value before the solute is added. Plotting $\ln\Delta$(emf) against time for the rating period should give a straight line, the slope of which equals $-k$.

The heat exchanged between the calorimeter and its surroundings during the experimental period is found by graphically integrating the values of $k(\Delta\text{emf})$ with respect to time from the time of the injection of the sample t_i to time t'. The result is converted into energy units by dividing by the electromotive power dE/dT and multiplying with the heat capacity of the calorimeter according to the equation:

$$Q = Cp \times dT/dE \times k \times \int_{t_i}^{t'} \Delta(\text{emf})dt \qquad [2]$$

To obtain the heat of solution, the heat for bringing the solute metal from 0°C to the temperature of the metal bath at the time t', must be subtracted from the total heat effect. The specific heats of the pure metals were taken from the literature[7] and the specific heat of the gold-silver alloy was calculated by the Kopp-Neumann rule, which has been shown to hold for this system.[8]

The calibration addition is calculated in a manner analogous to that for the solute additions with the difference that the value of the heat effect is known and the heat capacity of the calorimeter is found.

Experimental Results

Tables I and II list the integral heats of solution at 240°C and 300°C expressed in calories per gram-atom of solute; the compositions are stated as atomic percentage of solute in the solution formed. The heat of solution, ΔH, has a positive sign, if heat is absorbed. To obtain the integral heats of solution for the second, third, and fourth additions in each run, the heats of solution for all prior additions are added to the heat of solution of the addition under consideration and the total is referred to the total quantity of solute metal added.

Runs No. 11 and 12, from which the heats of solution in tin of the gold-silver alloy at 240°C were obtained, call for comment. In these runs identical quantities of tin were used and each addition consisted of the same amount of solute, but the first and third additions of run No. 11 and the second and fourth additions of run No. 12 had been annealed, whereas the other additions had been cold worked. The stored energy of cold working could be determined and has been reported.[7] To obtain the integral heats of solution stated in Table I the results for

Table I. Integral Heats of Solution of Gold, Silver, and Gold Silver Alloy in Tin at 240°C and for Different Resulting Compositions

Run No.	Solute	Resulting Composition, Atomic Pct Solute	Heat of Solution, ΔH, Cal per G-atom of Solute
17	Au	0.54	5990
		1.07	5960
		1.59	5980
		2.11	5960
2	Au	0.97	5710
		1.92	5620
		2.84	5530
		3.76	5440
11, 12	Alloy of 75% Au and 25% Ag	0.84	5330
		1.27	5240
		1.90	5350
		2.51	5360

annealed additions of run No. 11 were combined with those for the annealed additions of run No. 12. This combination was justified because the runs agreed within the uncertainty of observation.

In the composition range investigated, the integral heat of solution is approximately a linear function of the composition and may be extrapolated to infinite dilution. The resulting values are listed in Table III.

All measurements were made within 2° of 240° and 300°C. The results are reported for these even temperatures because over a range of 4° the heat of solution varies less than the uncertainty of the measurements.

Table IV gives the values of the observed heat effects for the additions of annealed alloy (runs No. 11 and 12) and for the mixtures of annealed gold and silver (run No. 13). Corresponding additions in these runs consisted of the same amount and overall composition of metal. The average of the values in Table IV yields a heat of formation of the 75 pct Au-25 pct Ag alloy of −1010 cal per g-atom of alloy at 0°C.

Discussion

Performance of Apparatus. The performance of the calorimeter in a given run could be judged by

Table II. Integral Heats of Solution of Gold, Silver, and Copper in Tin at 300°C for Different Resulting Compositions

Run No.	Solute	Resulting Composition, Atomic Pct Solute	Heat of Solution, ΔH, Cal per G-atom of Solute
18	Au	0.54	5610
		1.06	5630
		1.58	5620
		2.10	5560
21	Ag	0.36	4010
		0.73	3960
		1.09	4010
		1.44	3920
		1.81	3840
22	Ag	0.24	3870
		0.49	3860
		0.74	3850
		0.99	3840
		1.22	3830
20	Cu	0.53	2550
		1.07	2520
		1.59	2500
		2.12	2470

Table III. Integral Heats of Solution at Infinite Dilution of Gold, Silver, Gold-Silver Alloy, and Copper in Tin at 240° and 300° C

Run No.	Solute	Temperature, °C	Heat of solution, cal per g-atom of solute
11	Au	240	3060
12	Au	300	3010
2	Ag	240	3090
21, 22	Ag	300	3060
13, 23	30 Au-70 Ag	240	3120
26	Cu	300	2570

several indications. Among these were the time required for dissolution, the shape and slope of the plot of ln Δ(emf) vs. time, and the consistency of the results for the several additions of solute.

The time required for dissolution depended upon the nature, subdivision, and surface condition of the solute, the temperature of the metal bath, and the conditions at its surface. In the runs reported dissolution was completed within 4 min except in the silver run at 240°C and the copper run at 300°C, in which the times required for dissolution ranged up to 12 min. The four consecutive additions of copper, for example, required 5, 6, 8, and 10 min to dissolve. An increase in the time of dissolution makes the calculated heat effect less certain. At 240°C copper dissolved so slowly that the results were not considered reliable. On the other hand, the samples of gold-silver alloy dissolved within 1 min, which is one of several factors contributing toward the high precision of the values obtained.

Oxidation of the tin tended to interfere with the dissolution process, but could not be prevented entirely. The presence of more than a slight amount of tin oxide caused a skin to form across the surface of the liquid metal bath, on which the sample of added metal in some instances floated, although it had a greater density than tin. When this happened, the sample was insulated both thermally and chemically. Such difficulties occurred with calibration additions as well as solute additions and caused several runs to fail. If the stirrer was placed near the liquid metal surface in such a position as to break up the oxide skin, successful operation of the calorimeter was made possible in spite of slight oxidation.

Calculations. The heat exchanged between the calorimeter flask and its surroundings is less certain than the heat effect calculated from the temperature change within the metal bath. It is, therefore, desirable to make both calculations for as early a time after the solute addition as possible. On the other hand, the processes of dissolution and temperature equilization throughout the metal bath must be complete.

The plot of ln Δ(emf) vs. time should give a straight line if the calorimeter follows Newton's law. Nearly all plots, however, showed a slight decrease in slope in the interval from 5 to 25 min; thereafter the slope became fairly constant. The change in slope is attributed to a lag in establishing a steady-state temperature distribution in the walls of the Dewar flask. Thus more of the flask is slowly included as part of the calorimeter system, causing a slight increase in effective heat capacity with time.

The value of k was obtained as the slope of the curve of ln Δ(emf) vs. time, at time t' equal to 10 min after the addition of the sample. Since k often varied between additions as well as between runs, perhaps as a result of oxidation, the value of k measured for a given addition was used in the calculations of that addition. However, in the measurements on the gold-silver alloy and the mixture of gold and silver, the temperature change for the solute additions was so small that the k determined from the calibration addition was considered more dependable and was used in the calculations of all additions. The value of k for most runs ranged between 0.035 and 0.045 min^{-1}.

In the evaluation of heats of formation (and of retained energies of cold working) the values can be obtained directly from the observed heat effects by difference. The two runs, however, must be identical except for the condition of the solute. This is illustrated by runs No. 11, 12 and 13, as given in Table IV.

Precision. The consistency of the results within a given run can be judged by comparing the heats of solution for the consecutive additions. For the composition ranges covered the heat of solution should be a nearly linear function of the composition and deviations from linearity are assumed to be caused by experimental errors. The runs at 300°C show greater scattering than those at 240°C.

The difference between the results of runs No. 21 and 22 was about 150 cal per g-atom of silver dissolved while in runs No. 11 and 12, the difference was established to be less than 20 cal per g-atom of gold-silver alloy dissolved. In evaluating runs No. 21 and 22, the former is considered less reliable because of oxidation and is reported mainly to illustrate the effect of this operating difficulty on the measurements made. The high precision of the measurements made with the gold-silver alloy resulted from several factors. The time required for dissolution was less than 1 min. After dissolution the temperature change was less than 10 microvolts corresponding to ΔT less than 0.1°C and since the calorimeter exchanged heat very slowly, it was possible to estimate the Δ(emf) values to 0.5 microvolts.

Accuracy. The major sources of error were the determination of the temperature change in the calorimeter and the evaluation of the heat exchanged between the calorimeter and the salt bath. The Δ(emf) values ranged from 100 to 400 microvolts at time t' and probably are not in error by more than 2 microvolts or 2 pct. The additions of the gold-silver alloy and the mixture are exceptions, because the Δ(emf) values were probably correct to 1 microvolt.

The error in the evaluation of the heat exchanged with the salt bath results mainly from deviations in

Table IV. Observed Heat Effects for Runs No. 11, 12, and 13 and Heat of Formation of Gold-Silver Alloy

Addition	Run 11 (Alloy) Cal per g-atom	Run 12 (Alloy) Cal per g-atom	Run 13 (Mixture) Cal per g-atom	Heat of Formation by Difference, Cal per g-atom
1	147		272	3029
2		137	266	3019
3	160		312	3029
4		74	169	3001

the cooling of the calorimeter from Newton's law. That this error may be less than 1 pct is suggested by a special run in which two calibration additions of 4 and 8 g of tungsten yielded heat capacities of the calorimeter differing by less than 0.6 pct. The uncertainty in determining the slope at time τ was estimated to be about 3 pct. The errors in the Δ(emf) values used in the integration tended to cancel through the integration process.

Minor sources of error in the reported results were the uncertainty in the weights and purity of tin, tungsten, and solute metals, the change in composition due to oxidation of the metal bath and heat effects due to side reactions such as oxidation of the tin during the period of measurement. In addition, errors in determining the absolute temperature and errors in published values of the heat capacities of pure metals should be considered. An analysis of these errors indicates that they were negligible compared to the major errors already discussed.

Many of the errors affected both the calibration and solute additions in the same direction and to approximately the same extent and, therefore, their effects on the results are reduced.

The value of the total heat effect in the calorimeter is estimated to be accurate to about 5 pct. The heat required to raise the solute from 0°C to the temperature of the experiment is probably accurate to 0.5 pct. The following uncertainty limits in cal per g-atom are assigned to the heats of solution stated in the tables: gold, 200; silver and copper, 150; gold-silver alloy, 25. The uncertainty in the heat of formation is about 5 pct or 50 cal per g-atom.

Interpretation of Results: The absolute value of the integral heats of solution per gram-atom of solute may be expected to decrease linearly with increasing atomic percent solute in dilute solutions. A plot of the values listed in Tables I and II shows this behavior for silver and copper; the heat of solution of gold in tin is constant over the concentration range investigated and the slope of the heats of solution of the gold-silver alloy falls between those of the component metals.

The heats of solution of group IB metals at infinite dilution in tin (Table III) are not as similar as might be expected from the similarity of many of their properties. These differences in the heats of solution suggest that gold, silver, and copper differ markedly in their atomic interaction with tin as a solvent.

From the measured values of the heats of solution at infinite dilution and estimated values of the heat of fusion, the heat of mixing of liquid tin and undercooled liquid gold, silver, or copper can be estimated. The heat of fusion to form undercooled liquid at 300°C is calculated from the value at the melting point and the heat capacities of the solid and of the undercooled liquid. The estimates of the partial molar heats of mixing at 300°C are −8400 cal per g-atom of gold, +1250 cal per g-atom of silver, and −50 cal per g-atom of copper. The negligible heat of mixing for copper points to ideal solution behavior. The negative value for gold is consistent with the gold-tin phase diagram, which shows that this system has a strong tendency toward compound formation in the solid state.

Measurements of the electromotive force of galvanic cells consisting of liquid tin and gold-tin alloys containing at least 9 pct of gold show negative deviations of the activity of gold in tin from ideal behavior.[16] These results yield a partial molar heat of mixing in tin of −7100 cal per g-atom of gold at infinite dilution at 600°C. By a tenuous extrapolation to 600°C of the heats of solution determined in the investigation reported here and by estimating the heat of fusion of gold at this temperature, a partial molar heat of mixing at infinite dilution of −6700 cal per g-atom is found. On the basis of similar measurements on the tin-silver system,[17] a value of 5178.5 cal per g-atom of silver at infinite solution at 627°C has been reported; this value contrasts with a value of 1600 cal per g-atom estimated from the results reported here.

The value of the heat of formation at 0°C of the gold-silver alloy of −1010 cal per g-atom compares with a value of −890 cal per g-atom found for 500°C from data based on electromotive force measurements in galvanic cells.[18]

Summary

1—An isothermal calorimeter has been described which is suitable for measurements of heats of solution using liquid metal solvents in the temperature range from 150° to 320°C. Measurements may be made so as to yield other thermodynamic quantities such as heats of formation of alloys.

2—Integral heats of solution in liquid tin were measured at 240°C for gold, silver, and a gold-silver alloy and at 300°C for gold, silver, and copper as functions of the composition of the resulting solution. A linear relation was found in all cases over the composition ranges covered.

3—Heats of solution at infinite dilution were obtained by extrapolation.

4—The heat of formation of a 75 wt pct gold and 25 wt pct silver alloy at 0°C was determined.

Acknowledgments

The authors wish to express their sincere thanks to Professor Carl Wagner for much valuable advice. They are also indebted to Professors J. A. Beattie and John Chipman, who have contributed to this work in various ways. Thanks are due to the Central Research Dept. of the American Smelting and Refining Co. for providing high-purity copper wire. The work was performed under Contract No. AT-30-GEN-1002 with the AEC.

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Influence of Chemical Composition on the Rupture Properties At 1200°F of Wrought Cr-Ni-Co-Fe-Mo-W-Cb Alloys

By E. E. Reynolds, J. W. Freeman, and A. E. White

From a study of 63 systematic alloy modifications it was found that molybdenum, tungsten, and columbium, added individually or simultaneously, and increases in chromium cause major improvements in 1200°F rupture strengths of Cr-Ni-Co-Fe base alloys. Rupture strengths were a function of the effect of composition modifications on both the inherent creep resistance and the amount of deformation the alloy would tolerate before fracture.

THIS paper describes the results of an investigation of a series of alloys with systematic variations of the chemical composition of the following basic alloy: C, 0.15; Mn, 1.7; Si, 0.5; Cr, 20.0; Ni, 20.0; Co, 20.0; Mo, 3.0; W, 2.0; Cb, 1.0; N, 0.12; Fe, 32.0 pct. The 62 modifications of this alloy were produced under conditions which minimized all factors influencing properties at high temperatures except composition. Melting, fabrication, and heat treatment were carefully maintained constant. Stress-rupture properties at 1200°F were used as the primary criteria of evaluation of the alloy. The objective of the study was to obtain data for determining the fundamental role of the influence of alloying elements on properties of heat-resistant alloys at high temperatures. In addition the results should be useful in determining optimum chemical compositions, the sensitivity of properties to variations in composition, and the degree to which alloy content could be reduced while retaining worthwhile properties.

It is difficult or impossible to develop correlations between properties at high temperatures and systematic variations in chemical composition from published data for wrought heat-resistant alloys developed for gas turbines.[1-3] The main reason for this is the extreme dependence of the properties on conditions of treatment of the alloys.[4] In most cases variation in final treatments between alloys so influences the properties that the influence of chemical composition is obscured. In addition it is recognized that variations exist between heats of the same alloy which are related to melting practice and that there is a strong possibility that conditions of hot working influence response to final treatments.

Table I. Basic Alloy and Some Modifications Used

Element	Basic Alloy, Pct	Variations in Composition, Pct
C	0.15	0.08, 0.40, 0.60
Mn	1.7	0.03, 0.25, 0.50, 1.0, 2.5
Si	0.50	1.2, 1.6
Cr	20.0	10, 30
Ni	20.0	0, 10, 30
Co	20.0	0, 10, 30
Mo	3.0	0, 1, 2.5, 5, 7
W	2.0	0, 1, 5, 7
Cb	1.0	0, 2, 4, 6
N	0.12	0.004, 0.08, 0.18
Fe	32.0	

The development of heat-resistant alloys has been based on the gradual accumulation of data roughly related to composition from extensive testing programs. There is every reason to believe that in most cases the optimum compositions have been achieved by this procedure in the alloys commercially available. There are, however, very little data showing the influence of systematic variations of composition free from the influence of other factors, particularly for alloys of the type investigated. Several investigators of cast alloys have demonstrated compositional effects, notably Grant,[5] Epremian,[6] Guy,[7] and Harder and Gow.[8] Sykes[9] reviewed the work on the wrought alloy Rex 78 and the systematic variations of carbon, copper, molybdenum, and cobalt leading to the development of the stronger Rex 337A alloy. From the papers by Wilson[10] and Henry[11] it is possible to deduce the beneficial effect of substituting cobalt for iron in 0.45 pct C-20 pct Cr-20 pct Ni-4 pct Mo-4 pct W-4 pct Cb alloys. Wilson mentioned but did not present the extensive compositional studies involved in developing these alloys. Binder[12] showed optimum properties for 3, 2, and 1 pct, respectively, for molybdenum, tungsten, and columbium in 20 pct Cr-20 pct Ni-20 pct Co-30 pct Fe alloys for limited systematic variations of these

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elements in hot-worked bar stock. The same article, however, indicated the pronounced influence that variable hot-working conditions can have on the alloy. Since completion of the present study Harris and Child[7] have reported their work on the effect of carbide-forming elements on properties at 750° to 800°C (1382° to 1472°F) of Cr-Ni-Co-Fe alloys.

Procedure

Sixty-three alloys were investigated. Table I gives the basic alloy and some composition modifications used. In addition molybdenum, tungsten, and columbium were varied simultaneously from 0 to 4 pct in steps of 2 pct. Iron variations compensated for variations of total alloy content. For brevity a tabulation of the complete analyses is omitted.

Initial development of melting, forging, and heat treatment procedures to minimize all variable effects on properties except composition was done on the basic alloy. The reproducibility from heat to heat of rupture properties at 1200°F was the main criterion for final adoption of preparation procedures.

The alloys were melted as 9 lb induction furnace heats and poured into 9 in. tapered ingots. Ca-Si was used as a deoxidant. Care was taken to standardize melting practice for all the alloys. The effect of four deoxidation practices on properties was determined on the basic alloy. In addition to the standard Ca-Si deoxidation, heats were melted using no deoxidation, Zr-Si-Fe deoxidant, and a fluorspar slag.

The alloys were forged on a 400 lb capacity air hammer to 0.45 in. round bar stock in swaging dies. Preliminary forging experiments with varying techniques indicated that this swaging procedure was the easiest to control and reproduce. However, some of the alloys with variable carbon and manganese, made early in the program, were tested as square bar stock. Initial forging temperature was 2200°F with finishing temperatures above 1800°F as judged by color.

From previous investigation of the basic alloy[5] and preliminary experiments in this study, to find the treatment giving the best agreement in properties between heats, the following treatment was decided upon for all the experimental alloys: solution treated at 2200°F for 1 hr and water quenched plus aged at 1400°F for 24 hr and air cooled.

Vickers hardness and metallographic examinations were made on all the alloys. Electrolytic 10 pct chromic acid and water solution was used as an etchant.

The high temperature load carrying ability of the alloys was evaluated by stress-rupture properties at 1200°F. Rupture test specimens were 0.250 in. in diam with a 1 in. gage length. Tests of sufficient duration were made to establish the 100 hr rupture strengths and to permit at least an estimate of the 1000 hr strengths. Minimum creep rates were determined from time-elongation data taken during the rupture tests. The rupture strengths reported were established by double logarithmic curves of stress against the rupture time. Stresses causing given creep rates were obtained from double logarithmic curves of stress against minimum creep rate.

Reproducibility of Rupture Properties

The final objective of the work on techniques for preparing the experimental alloys was the development of a condition in which the rupture properties at 1200°F were reproducible from heat to heat of a given composition. Determination of significant property variations with chemical composition depends on the range of this reproducibility.

The rupture test characteristics at 1200°F for six heats of the basic alloy are given in Table II for both square and round bar stock. The range of reproducibility of rupture properties indicated for the round stock forged by the swaging procedure was as follows: 100 hr rupture strength, 48,000 to 50,000 psi; 1000 hr rupture strength, 37,000 to 38,000 psi; 100 hr rupture elongation, 19 to 25 pct. These ranges are used in interpretating the significant influences of composition variables for the materials forged as rounds. Properties of alloys with variable carbon and manganese, forged early in the program as square stock and tested as such, are compared with the wider property range indicated in Table II for square stock. Creep-rate stresses treated in a similar manner are also shown.

In addition Table II gives properties of alloys 74 and 75 which indicate that variation in deoxidation practice can have a pronounced effect on high temperature characteristics of alloys of this type. The influence on rupture test characteristics of changing hot-working and melting procedures indicates that the solution treatment of 2200°F did not completely eliminate variables in prior processing. Further, it is known that the solution plus 1400°F aging treatment used does not give maximum strengths for the basic alloy.[5] However, its use, plus the careful control of melting and forging conditions, is believed to have minimized all variable effects on properties except chemical composition in this investigation.

For comparative purposes the 1200°F rupture properties of two commercial heats of the basic alloy, solution treated and aged the same as the experimental alloys, are noted in Table II.

Microstructure

Microstructural studies were made of the alloys in the following conditions: as-cast; hot-forged;

Table II. Influence of Forging and Melting Variables on Rupture Test Characteristics at 1200°F of the Basic Alloy

Alloy	Rupture Strength, Psi		Estimated 100 Hr Rupture Elongation, Pct in 1 In.	Stress, Psi, to Cause Creep Rates of	
	100 Hr	1000 Hr		0.01 Pct per Hr	0.1 Pct per Hr
Final Adopted Forging Procedure — Round Bar Stock					
8	48,500	37,000	22	35,800	47,500
10	50,000	38,000	19	35,400	49,000
25	48,000	37,000	25	37,000	49,200
Average	48,800	37,300	22	36,000	47,600
Range	48,000 to 50,000	37,000 to 38,000	19 to 25	35,400 to 37,000	49,200 to 49,000
Preliminary Forging Procedure — Square Bar Stock					
7	48,500	37,000	20	35,800	46,300
9	46,500	36,000†	18	34,500	46,000
10	52,000	36,500	20	35,400	50,100
11	48,000	38,000	22	36,000	47,500
12	49,000	38,500	22	39,200	46,000
Average	48,000	37,200	20	36,000	47,200
Range	46,500 to 52,000	36,000 to 38,500	18 to 22	34,500 to 39,200	46,000 to 50,100
Variable Deoxidation Practice — Round Bar Stock					
74 (None)*	52,000	41,000†	16	40,700†	55,500†
75 (Zr-Si-Fe)*	55,000	40,500	18	42,300	57,600
Comparative Properties of Commercial Bar Stock of the Basic Alloy					
Heat 39276	50,000	42,000†	14		
A-1726	47,000	42,000†	16		

* Deoxidation practice:
Standard alloy — calcium-silicon deoxidant.
None — no deoxidation.
Zr-Si-Fe — zirconium-silicon-iron deoxidant.
† Estimated value.

Fig. 1a — Microstructure of basic alloy, heat 8, ingot as cast. Left, X100. Right, X1000.

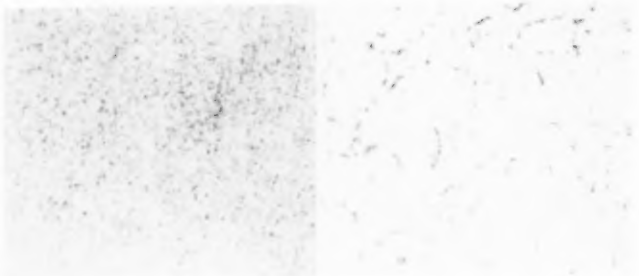


Fig. 1b — Microstructure of basic alloy, heat 8, as-forged 0.4 in. diam bar stock. Left, X100. Right, X1000.

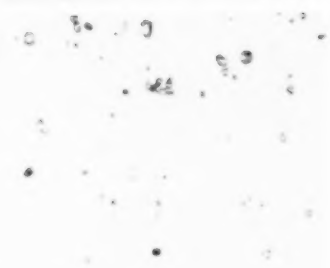


Fig. 1c — Microstructure of basic alloy, heat 8, solution treated 1 hr at 2200°F and water quenched. Left, X100. Right, X1000.

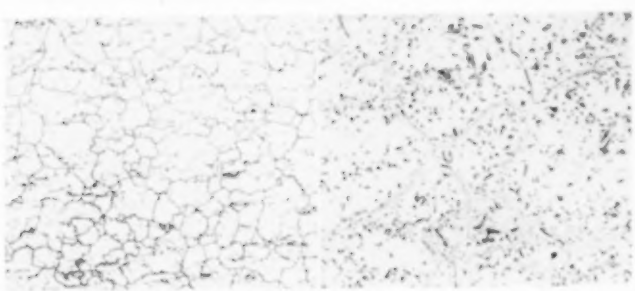


Fig. 1d — Microstructure of basic alloy, heat 8, solution treated and aged 24 hr at 1400°F. Left, X100. Right, X1000.

Fig. 1e — Microstructure of basic alloy, heat 8, rupture specimen. 499 hr for rupture at 1200°F under 40,000 psi. Left, X100. Right, X1000.

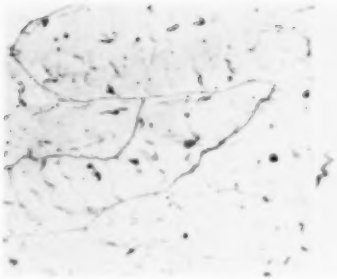


Fig. 2a — Effect on microstructure of omitting molybdenum, tungsten, and columbium from the basic analysis, alloy 43, ingot as cast. Left, X100. Right, X1000.

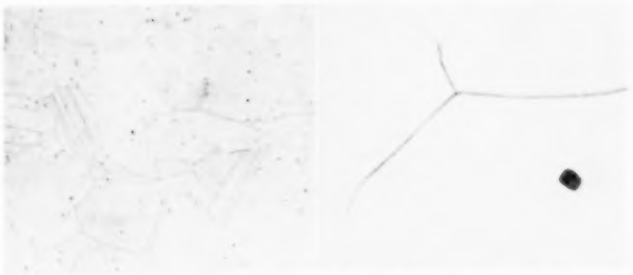


Fig. 2b — Effect on microstructure of omitting molybdenum, tungsten, and columbium from the basic analysis, alloy 43, solution treated 1 hr at 2200 F, water quenched. Left, X100. Right, X1000.

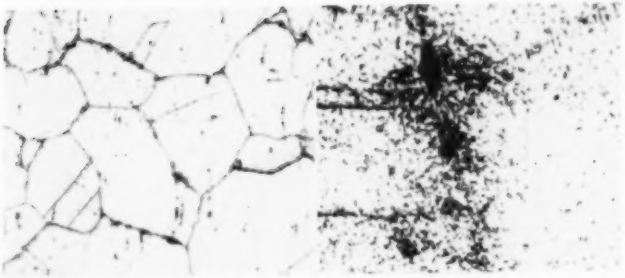


Fig. 2c — Effect on microstructure of omitting molybdenum, tungsten, and columbium from the basic analysis, alloy 43, solution treated and aged 24 hr at 1400 F. Left, X100. Right, X1000.

Fig. 2d — Effect on microstructure of omitting molybdenum, tungsten, and columbium from the basic analysis, alloy 43, rupture specimen, 819 hr for rupture at 1200 F under 20,000 psi. Left, X100. Right, X1000.

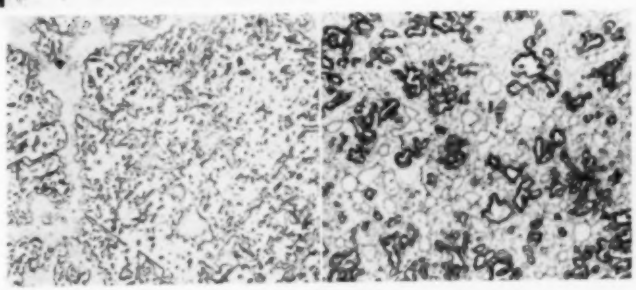
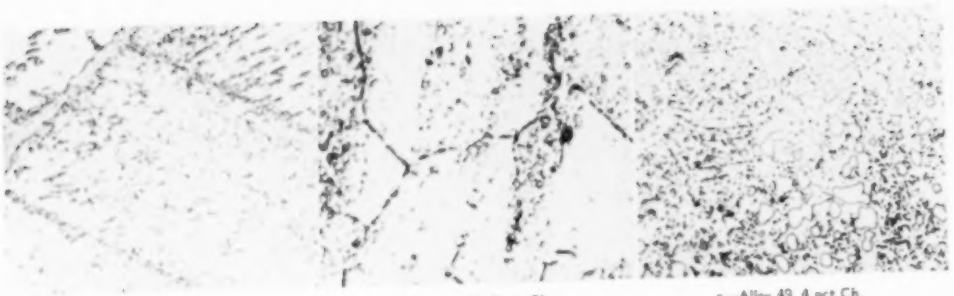


Fig. 3—Influence of carbon on microstructure. Heated 2200 F for 1 hr, water quenched, and heated at 1400 F for 24 hr. X1000. a (left)—Alloy 15, 0.40 pct C. b (right)—Alloy 16, 0.57 pct C.



a—Alloy 47, 0 pct Cb b—Alloy 48, 2 pct Cb c—Alloy 49, 4 pct Cb

Fig. 4—Influence of columbium on microstructure. Heated at 2200°F for 1 hr, water quenched, and heated at 1400°F for 24 hr. X1000

solution-treated 1 hr at 2200°F and water quenched; aged 24 hr at 1400°F after solution treatment; and rupture tested the longest time at 1200°F.

Effect of Treatment on Microstructure. The as-cast structure revealed the amount and distribution of the excess constituents in the cast dendritic pattern. The hot-forged structures were examined for flaws, uniformity of grain size, and distribution of excess constituents. Only limited information is included on the cast and forged structures, the main emphasis being placed on structures prior to testing in the heat-treated condition. The solution-treated structure showed the amount of insoluble excess constituents after light etching and grain size after deep etching. The aged structure revealed the amount and mode of grain boundary and matrix precipitation. From the structure of the longest time rupture test any change occurring during testing and the mode of fracture could be observed.

An example of microstructural variation with treatment for the basic alloy is shown in Fig. 1. The as-cast condition contained a considerable amount of excess constituent. After hot forging, the alloy was uniformly fine grained and contained excess constituent at the grain boundaries and in the matrix. Solution treating at 2200°F dissolved the grain boundary constituent but not the matrix constituent. Solution treating also coarsened the grains as best shown by the 1400°F aged structure. Aging caused much grain boundary precipitate and some random matrix precipitation. Rupture testing at 1200°F increased the matrix precipitate slightly.

As an example of one extreme to which microstructures varied with composition, Fig. 2 shows that the 0 pct Mo-0 pct W-0 pct Cb alloy differed from the standard alloy in that: There was much less excess constituent in the as-cast and the solution-treated conditions; grain size after solution treatment was much larger; and aging produced more precipitate near the grain boundaries and a preferred type of matrix precipitate which tended to follow definite crystallographic planes. The two alloys also differed in that the 0 pct Mo-0 pct W-0 pct Cb alloy had a completely intergranular fracture while that of the standard alloy was approximately half intergranular and half transgranular.

This comparison has pointed out the major similarities and differences in structures which were found for all the alloys. The similarities were:

1—The amount of excess constituent in the solution-treated condition was proportionate, for any given alloy, to the amount of excess constituent in the as-cast condition. The structures indicate that the rapid cooling of the ingot after solidification effectively solution treated the material.

2—All grain boundary constituents were dissolved during solution treatment.

3—Precipitation occurred during aging at 1400°F.

4—Very little additional precipitation occurred during rupture testing at 1200°F for any of the alloys with the exception of low cobalt modifications.

Major structural differences between the alloys were:

Table III. Summary of Influence of Alloying Elements on Increasing Tendency for Microstructural Changes

Alloying Element Varied	Composition Range, Pct	Insoluble Constituent Increase	Grain Size Decrease	Grain Boundary Precipitation Increase	Mode of Matrix Precipitation	Amount of Matrix Precipitation Increase
C	0.08-0.6	Strong	Mild	None	Random	Very strong
Mn	0.01-2.6	None	None	None	Random	None
Si	0.5-1.6	None	Mild	None	Random	Mild
Cr	10-20	None	Negative mild	Mild	Random	Strong
Co	20-70	None	Negative mild	None	Random to preferred	None*
Cu	0-16	Negative strong*	Negative mild	Negative weak	Random	None
Ti	0-10	Weak	None	None	Random	None
Ni	10-90	None	Negative mild	None	Random	Negative mild
Fe	0-92	None	Weak	None	Random†	Weak
Mo	0-4	None	Weak	None	Random†	Weak
W	0-4	None	Strong	Negative mild	Preferred to random	Negative mild
Cb	0-7	Strong	Mild	None	Random	Mild
Cb	1-4	Strong	None	None	Random	None
N	0.004-0.18	None				

* Ferrite phase in 0 pct Ni alloy in all conditions. A large amount of aging precipitate occurred in γ phase, but only a small amount in austenite matrix.

† Mode of precipitation not affected by molybdenum and tungsten. In alloys containing columbium the precipitate was random; without columbium the precipitate followed a preferred orientation.

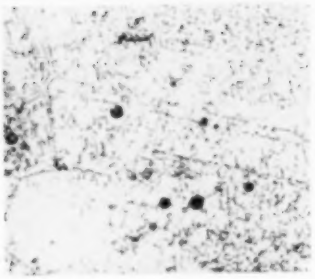


Fig. 5—Microstructure of alloy 52, 30 pct Cr. Heated at 2200° F for 1 hr, water quenched, and heated 1400° F for 24 hr. X1000.

1—Amount of excess constituent after solution treatment.

2—Grain size.

3—Location, type and amount of aging precipitate.

Influence of Alloying Elements on Microstructure: A summary of the effects of alloying elements on tendencies for microstructural changes is given in Table III. Two elements producing major microstructural changes were columbium and carbon (compare Figs. 3 and 4 with Fig. 1d). Both elements increased the amounts of insoluble constituent and aging precipitate and refined the grain size of solution-treated material. Columbium, in addition, changed the mode of matrix precipitation from internal crystallographic planes or preferred, when no columbium was present, to a random pattern, when 1 pct or more was present. Molybdenum and tungsten produced little change in microstructure except in alloys containing 4 pct Cb, in which case additions of these elements decreased the grain size and increased the matrix precipitation.

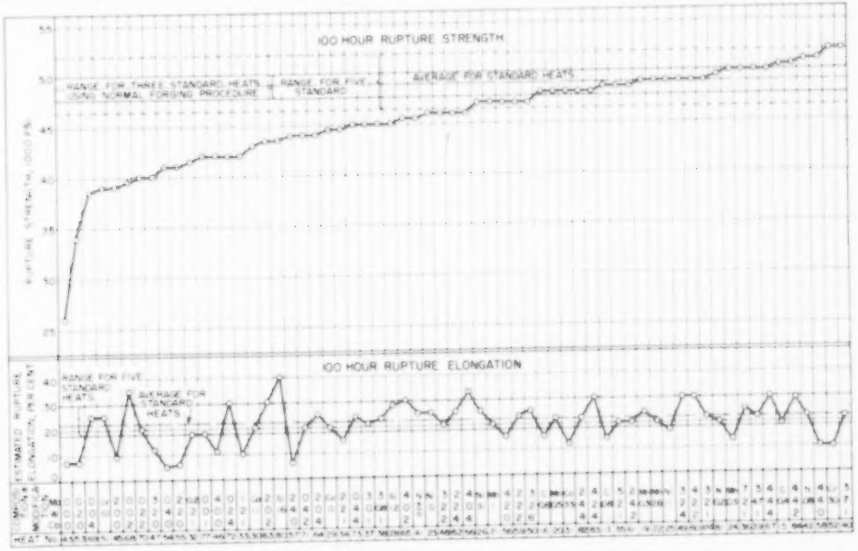
A chromium increase from 20 to 30 pct markedly increased the amount of aging precipitate and changed the mode of precipitation from random to preferred (compare Fig. 5 to Fig. 1d). Cobalt mildly increased grain size and decreased the amount of aging precipitate. Nickel between 10 and 30 pct produced only weak changes in structure. The 0 pct Ni alloy contained a ferrite-σ type of phase which disappeared when nickel was raised to 10 pct. Silicon slightly increased the amount of insoluble constituent and refined grain size. Manganese and nitrogen caused no discernible change in structure.

Hardness

Vickers hardness results at room temperature for the alloys in the solution-treated (2200° F) and the aged (1400° F) conditions will be briefly summarized. Additions of carbon, nitrogen, chromium, molybdenum, tungsten, and columbium tended to increase hardness in both conditions. Nickel, particularly from 0 to 10 pct, lowered hardness. Manganese, silicon, and cobalt did not appreciably affect hardness. Perhaps an exception to this was observed in the high (1.6 pct) silicon alloy. This was the only alloy of those studied which did not show any hardening as a result of aging. The addition of chromium from 20 to 30 pct markedly increased age-hardening characteristics. Additions of molybdenum or tungsten, while tending to increase hardness, did not appreciably increase the age-hardening tendency except for modifications containing more than 4 pct total of columbium plus tungsten or molybdenum. Additions of columbium from 0 to 2 pct narrowed the age-hardening range. Higher columbium additions, however, tended to broaden the age-hardening range for modifications containing larger amounts of molybdenum and tungsten.

Rupture-Test Characteristics

The 100 and 1000 hr rupture strengths (from double-logarithmic plots of stress against rupture time), 100 hr rupture elongation, and stresses for creep rates of 0.1 and 0.01 pct per hr (from double-logarithmic plots of stress against minimum creep


100 HOUR RUPTURE STRENGTH
RANGE FOR THREE STANDARD HEATS
RANGE FOR FIVE STANDARD HEATS
AVERAGE FOR STANDARD HEATS
100 HOUR RUPTURE ELONGATION
RANGE FOR FIVE STANDARD HEATS
AVERAGE FOR STANDARD HEATS

*ONLY THE DEVIATIONS FROM BASIC ANALYSIS SHOWN.
HEAT TREATMENT: 2200°F FOR 1 HOUR, WATER-QUENCHED, 1400°F FOR 24 HOURS, AIR COOLED.

Fig. 6—Influence of chemical composition on 100 hr rupture properties at 1200° F.

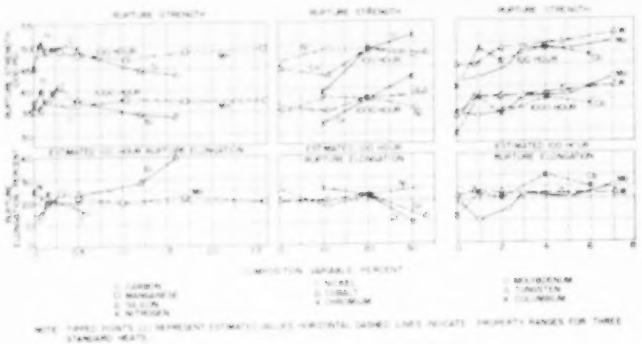


Fig. 7—Summary of the influence of variations of individual alloying elements on 100 hr and 1000 hr rupture strengths and 100 hr rupture elongations at 1200 F.

rates from the rupture tests) at 1200 F for all the alloys studied are given in Table IV. In this evaluation of the influence of chemical composition on properties most emphasis has been placed on rupture properties at 1200 F. Because the creep data were obtained from the rupture tests, it is emphasized that the rates of deformation were much higher than are usually associated with reported "creep strengths." The 100 hr rupture strengths and elongations for all the alloys are arranged in order of increasing strengths in Fig. 6. It is seen that the overall range in 100 hr strengths was from 26,000 to 52,000 psi. Elongations at rupture in 100 hr ranged from 5 to 40 pct. While in Fig. 6 there appears to be no relationship between rupture elongation and strength, it will be subsequently shown that such does exist.

Individual Variations of Elements: Fig. 7, which summarizes the rupture properties at 1200 F for individual variations of elements in the basic analysis, indicates the following influences of chemical composition:

1—Carbon and manganese had no appreciable influence over the ranges examined.

2—Very low nitrogen caused somewhat low rupture strength and intermediate nitrogen produced strengths slightly above normal.

3—Silicon was unique in that increasing amounts lowered rupture strength and increased elongation.

4—Increasing amounts of all other elements increased rupture strength over the complete range of variation with the exception of nickel, cobalt, and columbium. These elements apparently reached a saturation content for rupture strength at 10, 20, and 1 pct, respectively. Columbium additions caused a pronounced increase in rupture elongation.

5—Molybdenum and tungsten approached a saturation point at the 3 and 2 pct levels of the standard alloy although improvements were obtained by further additions of these elements. Molybdenum increased the elongation while tungsten had no effect.

6—Chromium markedly increased the rupture strength for additions from 10 to 30 pct, and decreased rupture elongation.

7—Relative magnitudes of 100 hr rupture strength improvements were: 20 pct Cr increased strength 13,000 psi; 7 pct Mo, 8500 psi; 7 pct W, 7000 psi; and 1 pct Cb, 8500 psi. The addition of 1 pct Si decreased strength 5000 psi.

The following modifications had strengths appreciably below that of the basic alloy: 1.2 pct Si; 1.6 Si; 10 Cr; 0 Co; 10 Co; 0 Mo; 1 Mo; 2 Mo; 0 W; 1 W; and 0 Cb. The only alloys which had appreciably higher strengths than the basic alloy were 30 pct Cr and 7 pct W. It is apparent that, in the single condition of treatment studied, rather wide individual variations of the elements can be permitted without appreciably altering properties, and chromium, cobalt, molybdenum, tungsten, and columbium are necessary for maintenance of properties similar to those of the basic alloy.

Simultaneous Variations of Molybdenum, Tungsten, and Columbium: In addition to the individual variations of all the elements already mentioned, the effects of simultaneous variations of molybdenum, tungsten, and columbium in steps of 2 pct from 0 to 4 pct were evaluated. The curves of Figs. 8, 9, and 10 show the influence on 100 hr rupture strength variations of one of these elements for ten different constant ratios of the other two.

Fig. 11 shows typical comparative influences of molybdenum, tungsten, and columbium on the 100 hr strength and elongation for three of the alloy modifications in which these elements were varied simultaneously: 0 pct Mo-0 pct W-0 pct Cb; 2 pct Mo-2 pct W-2 pct Cb; and 4 pct Mo-4 pct W-4 pct Cb. The effects of these elements were as follows:

1—The total absence of molybdenum, tungsten, and columbium in the basic analysis yielded an alloy with low rupture strength, 26,000 psi for rupture in 100 hr.

2—Separate additions of molybdenum, tungsten, or columbium in amounts up to 4 pct to the 0 pct Mo-0 pct W-0 pct Cb analysis raised the 100 hr rupture strength up to at least 40,000 psi as compared with 49,000 psi for the basic alloy.

3—Simultaneous additions of the three elements in amounts up to 4 pct at least doubled the strength of the 0 pct Mo-0 pct W-0 pct Cb analysis. Such additions did not, however, yield alloys with properties which were outstandingly better than those of the basic alloy.

4—Molybdenum and tungsten additions to 4 pct raised strength progressively. Additions of more than 1 pct Cb, however, were not beneficial to strength.

5—Molybdenum and tungsten had little effect on rupture elongation. Alloys containing no columbium had consistently low elongation and additions of 1 to 2 pct Cb markedly increased the elongation.

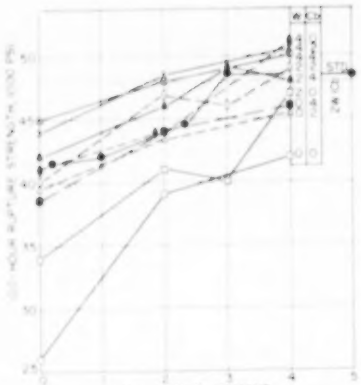
The influence of columbium on 100 hr rupture strength is further compared to that of molybdenum and tungsten in Fig. 12. Graphs at constant columbium contents of 0, 1, 2, and 4 pct indicate the combined strengthening influence of molybdenum plus tungsten. Curves representing this influence have been drawn and are summarized on the bottom

graph in which columbium content is the parameter. The dotted curves on the upper four graphs represent the influence of molybdenum and the dashed curves the influence of tungsten at constant amounts of the other element. Molybdenum is seen to have a greater strengthening influence when added in lower percentages and tungsten has the greater influence at higher percentages. These trends when combined strengthen the reliability of the single solid curves representing the data at constant columbium contents. More than 1 pct Cb was of no benefit to the alloys. When approximately 8 pct total Mo

Table IV. Rupture Test Characteristics at 1200 F for Modifications of the Basic Alloy

Alloy	Alloy Modifications, Pct*	Rupture Strength, Psi		Estimated 100 Hr Rupture Elongation, Pct in 1 In.	Stress to Cause Indicated Creep Rates, Psi	
		100 Hr	10000 Hr		0.01 Pct per Hr	0.1 Pct per Hr
Basic	(Range for round stock)	40,000 to 50,000	17,000 to 28,000	19 to 25	25,400 to 37,000	46,200 to 48,000
Basic	(Range for square stock)	46,500 to 52,000	26,000 to 28,500	18 to 22	34,500 to 38,200	46,000 to 50,100
15	0.08 C (sq)	48,500	26,000†	14	36,000†	47,000†
15	0.4 C (sq)	50,500	26,500	19	39,500	49,000
15	0.6 C (sq)	46,000	27,500	15	38,000	49,000†
16	0.6 C (rd)	48,000	27,000	15		
24	0.03 Mn (rd)	50,000	26,000†	13	39,000†	49,000
18	0.2 Mn (sq)	48,000	41,000†	24	39,000†	51,000
20	0.5 Mn (sq)	48,000	37,000†	22	36,000	47,000
21	1 Mn (sq)	47,000	36,000	20	39,000	48,000
22	2.6 Mn (sq)	49,000	27,500	20	25,000	
28	1.2 Si	45,000	34,500	28	33,700	43,000
80	1.6 Si	43,500	34,000†	40		43,000
31	10 Cr	39,000	32,000†	25	30,000†	38,000
32	20 Cr	52,000	42,500	10	42,000	37,000†
23	0 Ni	46,000	34,500	25	34,000	46,000
25	11 Ni	49,000	35,000	17	39,200	51,000
26	31 Ni	47,000	35,500†	25	32,500†	45,000
29	0.3 Co	44,500	36,000	20	34,500	43,500
30	11 Co	43,000	35,000	20	34,000	43,000
31	33 Co	48,000	39,000	12	39,000	49,000
32	0.2 Mo	41,500	34,000†	18	35,200	41,500
33	1.0 Mo	42,000	33,500†	10	35,000	44,500
34	2.3 Mo	44,500	34,500†	15	36,000†	44,000†
35	3.0 Mo	46,500	38,000†	20	37,000†	48,000
36	7.9 Mo	50,000	42,000†	25	38,000†	50,000
37	0 W	45,000	33,500†	21	34,000†	44,500†
38	0.8 W	45,000	37,500†	23	35,500†	46,500†
39	4.7 W	50,000	39,000†	22	38,000†	50,500†
40	7.1 W	52,000	40,000†	22	38,000†	50,500
47	0 Cb	40,000	29,500†	12	33,500	44,500
48	2 Cb	46,000	34,000†	20	35,500	44,500
49	4 Cb	49,000	37,500†	20	36,000	48,000
50	6 Cb	47,000	36,000	23	35,000	46,500
41	0.004 N	45,500	36,500†	25	35,000†	46,500†
42	0.08 N	51,000	40,000†	22	38,000†	50,000
61	0.18 N	49,500	39,000†	20	38,000†	49,000†
43	0 Mo 0 W 6 Cb	26,000	19,500†	7	25,500	
45	2 Mo 0 W 6 Cb	39,000	27,500	9	33,000	44,000†
46	4 Mo 0 W 6 Cb	42,000	30,500†	11	34,100	45,000
53	0 Mo 2 W 6 Cb	34,000	26,000	7	30,000	37,700
54	0 Mo 4 W 6 Cb	41,000	32,000†	5	38,200	50,500†
55	2 Mo 2 W 6 Cb	41,000	32,000†	6	36,000	45,500†
56	4 Mo 2 W 6 Cb	47,000	38,000	15	39,000	47,500
57	2 Mo 4 W 6 Cb	44,000†	33,000†	6	40,000	49,000†
58	4 Mo 4 W 6 Cb	51,000	40,000	10	40,000	55,000
59	2 Mo 2 W 2 Cb	47,000	36,000†	23	37,000†	44,000
60	4 Mo 2 W 2 Cb	49,000	41,000†	20	40,500†	47,500
61	2 Mo 4 W 2 Cb	49,500	48,000†	20	37,500†	49,000†
62	2 Mo 2 W 4 Cb	46,000	34,000†	25	36,500†	45,000
63	2 Mo 0 W 2 Cb	43,500	34,000†	30	33,600	43,500
64	2 Mo 0 W 4 Cb	44,000	34,000†	25		41,000
65	4 Mo 0 W 2 Cb	45,500	37,000†	30	35,000†	44,000
66	4 Mo 0 W 4 Cb	48,000	36,500†	33	35,000†	45,000†
67	4 Mo 4 W 4 Cb	50,000	38,000	30	36,000	47,500
77	0 Mo 0 W 1 Cb	42,000	31,000†	18	30,000†	42,500
68	0 Mo 0 W 2 Cb	39,500	31,500†	35	31,500†	38,000
69	0 Mo 0 W 4 Cb	38,500	30,500†	25	31,500†	37,500
70	0 Mo 2 W 2 Cb	40,000	32,000†	20	32,000	39,200
71	0 Mo 4 W 2 Cb	43,000	37,000†	20	38,000	43,800
72	0 Mo 2 W 4 Cb	42,000	32,500†	30	34,000	40,500†
73	0 Mo 4 W 4 Cb	45,000	36,500†	24	38,000	43,800
82	2 Mo 4 W 4 Cb	48,000	37,000†	22	35,000	46,000
83	4 Mo 2 W 4 Cb	46,000	36,000†	20	34,000†	44,500
84	4 Mo 4 W 2 Cb	50,500	39,500	29	37,000	48,500

* Square — forged as square bar.
Round — forged as round bar.
All alloys higher than 22 were forged as round bars only.
† Estimated by extrapolation of log-log plots of at least 3 test points.



NOTE: HORIZONTAL DASHED LINES INDICATE PROPERTY RANGE FOR THREE STANDARD HEATS

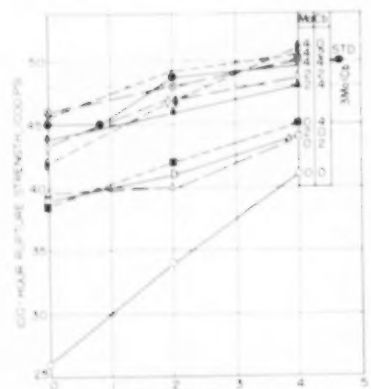
Fig. 8—Summary of influence of molybdenum on 100 hr rupture strength at 1200 F of ten W-Cb modifications.

plus W was present, any addition of columbium was of no benefit to the strength. As has been noted previously, however, columbium additions of 1 pct markedly improved the rupture ductility over that of the 0 pct Cb alloys, regardless of the influence of columbium on strength.

Subject to the limitation of only one condition of preparation it is possible to predict from the summary of curves of Fig. 12 the 100 hr rupture strength of alloys with any combination of molybdenum, tungsten, and columbium within the composition ranges investigated.

Interrelation of Rupture, Creep, and Elongation

The main reason for considering creep data from time-elongation curves of the rupture tests was to determine, if possible, how changes in composition affected a change in rupture strength. It is observed from Table IV that, in general, the stresses to cause a minimum creep rate of 0.1 pct per hr were of the

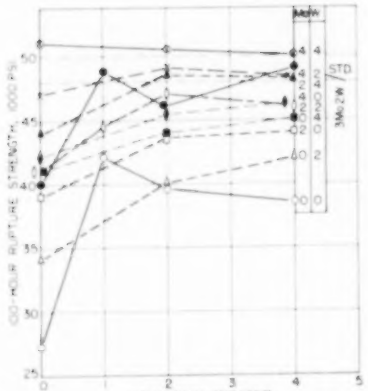


NOTE: HORIZONTAL DASHED LINES INDICATE PROPERTY RANGE FOR THREE STANDARD HEATS

Fig. 9—Summary of influence of tungsten on 100 hr rupture strength at 1200 F of ten Mo-Cb modifications.

same order of magnitude and followed the same trends with composition variation as the 100 hr rupture strengths. The main exception to this was in alloys in which columbium was systematically varied from 0 to 4 pct. In this case the stresses at constant creep rate remained constant or decreased with increasing rupture strength.

Fig. 13 shows for all the alloys studied the variation of the 100 hr rupture strength with stress to cause a creep rate of 0.1 pct per hr. Average curves are drawn representing the points for the low (5 to 10 pct), intermediate (11 to 19 pct), and high (20 to 40 pct) 100 hr rupture elongation levels encountered. While there are ranges for the rupture-creep property relations, it is noted that the range representing high elongations is definitely at a higher level than that representing low elongation. The range for intermediate elongations overlaps both those for high and low elongations. These ranges, while partially the result of variation in actual elongation within the range, particularly at the lower elonga-



NOTE: HORIZONTAL DASHED LINES INDICATE PROPERTY RANGE FOR THREE STANDARD HEATS

Fig. 10—Summary of influence of columbium on 100 hr rupture strength at 1200 F of ten Mo-W modifications.

tions, are believed to be mainly caused by the limitation of the reproducibility of properties from heat to heat of a given analysis and by the fact that the creep properties in many cases were estimated from only a small amount of time-elongation data. Another probable cause for the ranges could be that in certain alloys the stress for constant creep rate is not an accurate representation of the creep resistance.

In general it appears, however, that the stress to cause a minimum rate of 0.1 pct per hr is a measure of creep resistance which controls the 100 hr rupture strength. The relation is linear and represented by a line with a slope of approximately 45°. The level of rupture properties at a given creep resistance, however, is dependent upon inherent ability of the alloys to deform before fracture.

It is noted in Fig. 13 that the level of the relation between rupture strength and creep resistance is dependent on total elongation only when this elongation changes from low to high. The reason for this is the difference between the time-elongation curves for ductile and brittle materials. Ductile materials toward the end of the period of increasing creep rate

(third stage creep) deform a large amount in a very short time period. The elongation near the end of the test has relatively small time dependence and thus little influence on the rupture time. Brittle materials, on the other hand, elongate more gradually with time near the end of the test. Thus with the same creep resistance the rupture time is more dependent on the relative inherent ability of the materials to deform before fracture.

The solid points in Fig. 13, indicating elongations between 5 and 10 pct, represent the alloys which did not contain columbium. One point at the highest stress represents the high chromium alloy which had low ductility. It is evident that the apparent lack of correlation between creep and rupture properties observed for alloys in which columbium was varied systematically resulted from the added influence of total elongation on rupture strength caused by columbium.

It can be concluded that the rupture strength variations with chemical composition observed in this investigation resulted from changes in inherent creep resistance caused by alloy additions except for

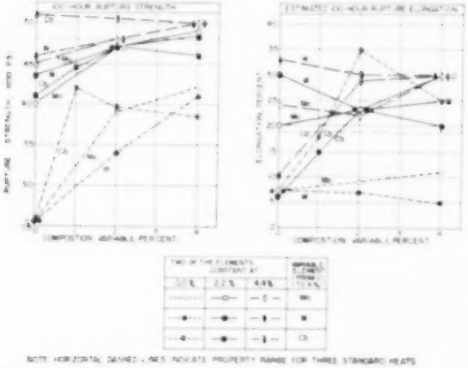


Fig. 11—Comparative influence of molybdenum, tungsten, and columbium on 100 hr rupture properties at 1200 F.

those in which total elongation to fracture changed from low (5 to 10 pct) to high (above approximately 20 pct) values. In such cases the relative ability to deform before fracture also influenced the rupture strength.

Interpretation of the Influence of Composition on Rupture Properties

The results indicate that by careful control of processing conditions the high temperature characteristics of wrought Cr-Ni-Co-Fe-Mo-W-Cb alloys can be related to systematic variations in chemical composition and that major changes in rupture characteristics at 1200 F accompany certain variations in composition. Summaries of this influence on 100 hr rupture strengths were given in Figs. 7 and 12. Interpretation of the manner in which the composition influences high temperature properties of these alloys by controlling the inherent creep resistance and the ability to deform before fracture can be made in view of simultaneous effects noted in other metallurgical characteristics. The following observations of such effects were made:

1—Only nine alloys of the 63 different compositions studied developed a pronounced amount of visible microstructural precipitate during aging as

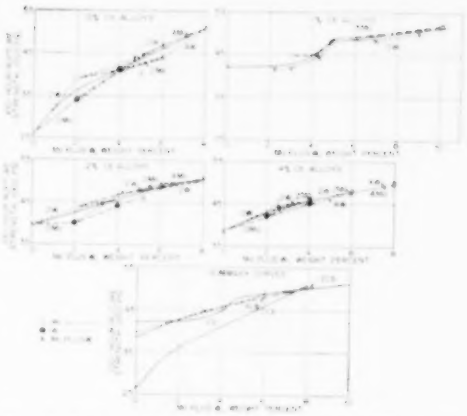


Fig. 12—Influence of molybdenum and tungsten additions on a total weight percentage basis on 100 hr rupture strength at 1200 F of columbium modifications.

shown in Table V. Except for the 30 pct Cr alloy, the additional microstructural precipitate, resulting from either increased carbon or columbium or decreased cobalt, did not have any apparent beneficial effect on strength. The matrix precipitate which occurred during aging of the 30 pct Cr alloy was of a different type than that of other alloys with heavy precipitation, being preferred rather than random. The hardness increase during aging of this alloy was exceptionally high. Thus the substantial strength increase with the addition of chromium from 20 to 30 pct appeared to result, at least in part, from the aging characteristics caused by higher chromium.

2—Systematic additions of molybdenum and tungsten up to 4 pct total did not affect the amount of visible precipitate occurring during aging of alloys containing less than 4 pct Cb. Creep resistance and rupture strength improved systematically with these additions over the entire composition range, both in

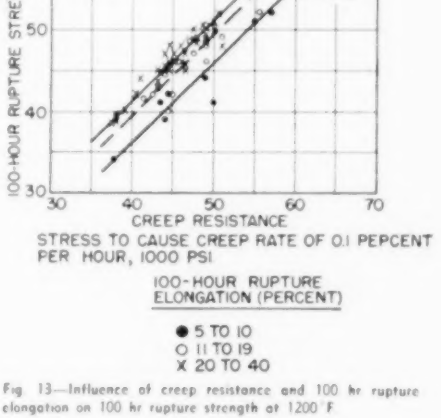


Fig. 13—Influence of creep resistance and 100 hr rupture elongation on 100 hr rupture strength at 1200 F.

the absence and presence of increased amounts of visible aging precipitate. The high Mo-W-Cb alloys did not develop an appreciable relative increase in hardness during aging and had a random matrix precipitate. It thus appears that molybdenum and tungsten cause strengthening by entering solid solution, rather than by aging effects.

3—Columbium produced its major improvement in rupture strength in additions of 1 pct to the 0 pct Cb alloys. This improvement was shown to be the result of the higher ductility caused by columbium rather than an improvement in creep resistance, which columbium additions either did not change or reduced. Additions of more than 2 pct Cb did not add anything to rupture strength because creep resistance was not increased and the rupture elongations were all at a high level where changes in total elongation did not appreciably affect fracture time. Microstructural examinations indicated that columbium, or the compound it caused to form, was at most only partially soluble at temperatures up to 2200 F. This limited solubility evidently was the reason that there was no improvement in creep resistance when columbium was added.

4—There were certain similarities between the effects of carbon and columbium on the amount of excess constituents present in the microstructures. While the excess constituents resulting from carbon and columbium additions were not necessarily the same phases, the appearance of large amounts, both in the solution-treated condition and precipitated during aging of the high carbon modifications, had little affect on properties as was also the case for high columbium alloys. Carbon apparently combines with elements normally present in the solid solution to form certain of the observed excess constituents. In view of this the inherent matrix strength of the material should be reduced. This effect appeared to be the case for the 0.60 pct C alloy which did show a tendency toward lower strength. However, balancing factors, which could hold strength up to a certain extent, could be that some strengthening resulted from the very heavy aging precipitation, or that carbon did not combine with the major elements which increased the strength.

5—Cobalt additions from 0 to 20 pct, which tended to raise creep resistance and thus rupture strength of the alloy, decreased the amount of visible aging precipitate, apparently increasing the solubility of the strengthening elements. A similar effect of cobalt was observed by Sykes.[7] Further addition to 33 pct Co increased creep resistance but did not appreciably improve rupture strength because of the lower rupture elongation.

6—The major strengthening effect of nickel was between 0 and 10 pct. This addition changed the alloy from an unbalanced ferrite-austenite composition of the 0 pct Ni alloy to the austenitic-matrix type alloy typical of all the other alloys studied. By preventing the formation of the weak ferrite-σ type phase, 10 pct Ni caused the elements in this phase to enter the solid solution of the matrix, thus increasing the creep resistance and rupture strength.

Table V. Composition of Alloys Which Developed Visible Microstructural Precipitate During Aging

Alloy No.	Composition Variable, Pct
13	0.4 C
16	0.6 C
28	10 Ni
29	0 Ni
49	2Mo–2W–4Cb
50	2Mo–2W–6Cb
52	2Mo–4W–4Cb
53	4Mo–2W–4Cb
61	4Mo–4W–4Cb

Each of these observations of the relations of metallurgical characteristics and high temperature properties points to the conclusion that the major strengthening effects produced by alloy variations in this investigation were the result of the elements entering into solid solution in the alloys. The two outstanding examples of solid solution strengthening were associated with molybdenum and tungsten. These elements would enter the solid solution by substitution, as also would chromium, nickel, and cobalt for atoms of iron. The atoms of these elements are all about the same size and could substitutionally enter the crystal lattice with ease. Substitution of the larger or incongruous atoms of molybdenum and tungsten into the lattice, however, would necessarily set up a strained condition. Such strains in the lattice interfere with the flow conditions during creep, thus giving the material higher creep resistance. The role of columbium, which also has relatively large atoms, is complicated by the high affinity of columbium for carbon and by the apparent low limit of solubility of columbium, or the phase which it forms. The substitution of the similar sized elements, chromium, nickel, or cobalt, into the lattice would not set up particularly strained conditions and thus strengthening from solid-solution effects would not result. This has also been demonstrated by a recent investigation of Fe-Cr-Ni alloys.[8] The effects of nickel and cobalt on properties and microstructure appeared to be the result of these elements either increasing the matrix solubility for other elements (the two most probable being molybdenum and tungsten) or by increasing the resistance to relaxation of internal strain in the matrix. Chromium, as noted, apparently increased strength, at least in part, by aging effects.

It would appear therefore that as the number of incongruous atoms entering solid solution increased, the strength should increase proportionately. The modifications in which molybdenum and tungsten additions caused strength increases were pointed out as examples of strengthening as a result of solution effects. Fig. 14 shows the influence on the 100 hr rupture strength of total atomic additions of molybdenum and tungsten to alloys containing four levels of columbium. This figure is similar to the presentation in Fig. 12 of the same data on a weight percentage basis. Trends in the summary curves, with columbium content as a parameter, are the same in both presentations; columbium above 1 pct being of no benefit to strength. In general, the curves in Fig. 14 show a continuous and approximately proportionate increase in strength with atomic additions of molybdenum and tungsten. This is consistent with what would be expected if solid solution effects are responsible for the strength increase.

The points on the graphs of Fig. 14 have been connected so as to show the comparative effects of molybdenum and tungsten, the dotted lines showing the molybdenum effects and the dashed lines the tungsten effects. Although the average solid-line curves drawn do represent quite well the data on the graphs, there is an indication that additions of atoms of tungsten to the solid solution in general had a greater strengthening effect than equivalent atomic additions of molybdenum.

In addition to the 30 pct Cr alloy, another exception, which does not agree with the indication that strengthening resulted from solid solution effects, was that encountered in the influence of silicon variations. The effect of silicon, varied from 0.5 to 1.6 pct, was to markedly lower strength properties and increase total deformation to fracture. There was only slight change in microstructure produced by silicon. It was also observed that the high silicon alloy was the only alloy of all those studied which did not show any increase in hardness during aging. A clue to this apparently anomalous effect of silicon is to be found in the results of the effect of deoxidation practice during melting on the properties of the basic alloy. Table II shows a 100 hr rupture strength of 52,000 psi for alloy 74 which was not deoxidized before pouring. This strength is to be compared with the strength range of 48,000 to 50,000 psi for the standard alloy deoxidized in the normal manner with Ca-Si deoxidant and with the 56,000 psi rupture strength of alloy 75 which was deoxidized with Zr-Si-Fe deoxidant. These results indicate that a marked influence may occur on properties of a given alloy as a result of variation of melting procedure. Silicon is an element which definitely plays an important role in melting, particularly in deoxidation practice. It thus appears that inherent characteristics imparted to the material during melting, not removed by subsequent processing nor evident in microstructure, could be responsible for the unusually low strengths of the high silicon alloys.

The basic alloy has been shown by previous investigations to be an alloy which does not develop appreciable strengthening at high temperatures as a result of visible precipitation reactions during aging after solution treatment.[7] Evidence presented in this discussion indicates that the major strengthening effects accounting for the good strength of this alloy result from additions of incongruous atoms of elements to the solid solution lattice of the austenite-type matrix.

It is recognized that this interpretation of results is tempered by the limitations placed on the investigation. These were: The limited number of composition variables studied; the use of only one condition of processing; the evaluation of high temperature characteristics by only relatively short time rupture tests at 1200°F; and the use of only microstructural and hardness data to provide additional metallurgical information.

Optimum Alloy Content and Composition Ranges

In addition to the main objective of determining the influence of chemical composition variations on rupture properties at 1200°F, the present investigation was also intended as an initial step toward establishment of optimum compositions for Cr-Ni-Co-Fe-Mo-W-Cb alloys. While the overall property range was quite wide and information was obtained concerning the influence of each element on properties, no alloy had properties which were outstanding compared to those of the standard analysis of the basic alloy. It was shown that most of the elements present in this analysis are necessary to yield satisfactory properties, but the elements could be varied individually over relatively wide ranges in the basic analysis without appreciably altering properties. Indications are that nickel can be varied from 11 to 20 pct, carbon from 0.08 to 0.40 pct, cobalt from 20 to 33 pct, columbium from 1 to 4 pct, manganese from 0.3 to 2.6 pct, and nitrogen from 0.08 to 0.18

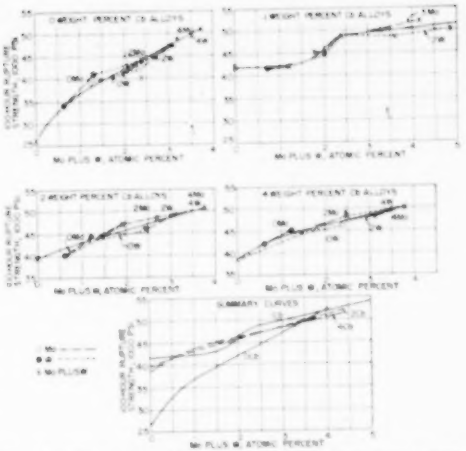


Fig. 14—Influence of molybdenum and tungsten additions on a total atomic percentage basis on 100 hr rupture strength at 1200°F of columbium modifications.

pct in the basic analysis without appreciably affecting properties. It was also shown that chromium, molybdenum, and tungsten are necessary for maintenance of properties and that columbium in additions not beyond 1 pct is necessary for high ductility characteristics. It is possible, however, to obtain strengths as high or higher than that of the basic alloy without the use of columbium by increasing molybdenum and tungsten.

Nature of Phases

As yet little is known concerning the nature of the phases present in alloys of the type investigated. It is generally accepted that the austentite-type matrix is a solid solution which is saturated with respect to certain unidentified constituents at both the solution and aging temperatures. It is also known that columbium, chromium, molybdenum, and tungsten are prone to form carbides or nitrides under certain conditions, and that intermetallic compounds, such as the Fe-Cr σ phase, and also a ferrite-type phase, are possible microconstituents.

In this investigation there was evidence that carbon entered into the reaction forming the phase which was at least partially insoluble at the solution treatment temperature and that columbium was the other significant element in the formation of this phase. Carbon also appeared to be an important component of the precipitate which occurred during aging.

Chromium evidently contributed to the formation of the phase which precipitated during aging of the 0 pct Mo-0 pct W-0 pct Cb alloy. It appeared that chromium was also quite important in the aging reaction in the 0 pct Cb alloys since additions of molybdenum and tungsten to these alloys did not change the appearance or appreciably affect the amount of aging precipitate.

Columbium additions from 2 to 4 pct in alloys containing high molybdenum plus tungsten appreciably increased the amount of aging precipitate. Evidently this resulted from exceeding the solubility limit causing the rejection during aging of the excess phase from supersaturated solution. The nature of this phase was not evident from the data, although

there was some indication that molybdenum and tungsten, which apparently increased strength by substitutional entrance into solid solution, probably were not present in the precipitate. The two examples of this were:

1—Additions of carbon to the basic alloy increased aging precipitate but did not appreciably lower strength as would be expected if molybdenum or tungsten were taken out of solution.

2—Additions of columbium from 2 to 4 pct in alloys also containing at least 6 pct total Mo plus W did not affect strength appreciably while increasing the amount of aging precipitate. On the other hand, when molybdenum or tungsten were raised from 2 to 4 pct in alloys containing 4 pct Cb, producing alloys with more aging precipitate, the strength was improved, indicating that molybdenum and tungsten went into solution. In this event it is probable that chromium, or some of the other elements of similar atomic size, were forced out of solution as carbides or intermetallic compounds.

On the basis of the composition range studied for nitrogen, it did not appear that this element appreciably affected the microconstituents.

Summary

By the use of careful control over processing conditions this investigation has shown that it is possible to correlate the 1200 F stress-rupture properties of wrought Cr-Ni-Co-Fe-Mo-W-Cb alloys with systematic variations in chemical composition and that a wide range in properties can be obtained by such variations. Major strengthening effects resulted from additions of chromium, molybdenum, tungsten, and columbium.

Subject to the limitations placed on this investigation by microstructural hardness and 1200 F rupture studies of a limited number of modifications in only one condition of processing, the following findings were made:

1—Carbon (varied from 0.08 to 0.6 pct), manganese (0.3 to 2.6 pct), nitrogen (0.08 to 0.18 pct), nickel (11 to 20 pct), cobalt (20 to 33 pct), and columbium (2 to 4 pct) do not appreciably influence 1200 F rupture properties. Nitrogen (0.004 to 0.08 pct), chromium (10 to 30 pct), nickel (0 to 11 pct), cobalt (0 to 20 pct), molybdenum (0 to 4 pct), tungsten (0 to 4 pct), and columbium (0 to 1 pct) improve the rupture strength. Silicon (0.5 to 1.6 pct) and nickel (20 to 30 pct) lower rupture strength.

2—The rupture strength variations with chemical composition observed in this investigation were the result of changes in inherent creep resistance, caused by alloy additions, except for composition variations for which total elongation to fracture changed from very low (below 10 pct) to high (above approximately 20 pct), in which case the greater ability to deform before fracture also improved the rupture strength.

3—The rupture strength improvements accompanying the increased creep resistance with additions of molybdenum and tungsten are the result of the strengthening influence of these incongruous atoms entering substitutionally into the matrix solid solution. Nickel and cobalt additions apparently improve creep resistance by increasing the solubility of molybdenum and tungsten. The increased creep resistance produced by chromium additions apparently results, at least in part, from an aging reaction. The creep resistance is not appreciably influenced by columbium. Improvements in rupture strength with small additions of columbium result from the greater ability to deform before fracture of alloys containing columbium. The detrimental effect of silicon on strength properties is possibly connected with melting phenomena which are not yet understood.

4—Columbium, chromium, and carbon produce major changes in microstructure. There is limited evidence to indicate that these are the major elements present in the excess constituents in the structure of the alloys.

Acknowledgments

The authors wish to express appreciation to the National Advisory Committee for Aeronautics for their financial support of this work as part of their program of sponsored research on heat-resisting alloys at the Engineering Research Institute of the University of Michigan, and for their permission to publish this paper. A more complete report on this investigation has been issued by the NACA under reference 17. The assistance of William Telfer in development of a forging technique for the experimental alloys is gratefully acknowledged.

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Creep Correlations in Alpha Solid Solutions of Aluminum

by Oleg D. Sherby and John E. Dorn

SEVERAL years ago Zener and Hollomon[1] suggested that the flow stress of metals might be related to the temperature and strain rate in accord with the functional equation:

$$\sigma = \sigma\,(\dot{\epsilon}\, e^{+\Delta H/RT}) \qquad [1]$$

at the same state.

The Zener-Hollomon relation also contains the significant tacit implication that the energy for activation, ΔH, is substantially independent of the state of the material.

The utility of this method for correlating creep data with tensile data was illustrated in a preliminary report[2] on the effect of alloying additions on the secondary creep rates of binary α solid solutions in aluminum as shown for Al-Mg alloys in Fig. 1. Not only do the secondary creep and ultimate tensile properties for each alloy correlate well on this plot but in addition the activation energy, $\Delta H = 17{,}900$ R cal per mol, is identical for the various compositions. Similar types of curves correlating the secondary creep rates at 422° K (300° F) with ultimate tensile data were also obtained for a series of dilute α solid solutions of copper, germanium, zinc, and silver in aluminum. In all cases the activation energy for creep, ΔH, was found to be equal to about 17,900 R cal per mol independent of the type of alloying element or its concentration. The coincidence of the activation energies for these alloys is probably due to the fact that the activation energies for creep are rather insensitive to small composition changes. Alloying additions, as shown in Fig. 1, however, increased the stress necessary to obtain equivalent values of $\dot{\epsilon}e^{+\Delta H/RT}$. Thus the stress level in curves of the type represented by Fig. 1 gives the relative creep strengths of the various alloys.

Inasmuch as these correlations between creep and tensile data were obtained for creep tests at 422° K, it appeared advisable to ascertain the range of secondary creep rates and temperatures over which correlations between creep and tensile data could be made on the basis of the Zener-Hollomon relationship. If, for example, the activation energy changes with different ranges of creep temperatures, the utility of the proposed analysis would be severely weakened. But if ΔH is constant not only for all dilute alloys, but also over wide ranges of temperature and secondary creep rates, confidence will be developed not only in the broad utility of the Zener-Hollomon relationship, but also in its theoretical justification. The following investigation was instituted in order to ascertain the range of validity of the Zener-Hollomon relationship when it is applied to creep and tension data.

Table I. Chemical Analysis and Grain Size of Alloys

Alloying Element	Atomic Pct	Residual Impurities, Wt Pct					Mean Grain Diameter, mm
		Si	Fe	Cu	Mg	Mn	
Aluminum	99.997	0.001	0.003	0.006	0.001		0.23
Magnesium	1.617	0.001	0.004	0.006			0.26
Copper	0.101	0.002	0.003		0.0006	0.001	0.29
Zinc	1.876	0.002	0.005	0.007	0.001		0.26

* The authors express their appreciation to the Aluminum Company of America for the preparation and chemical analyses of these alloys.

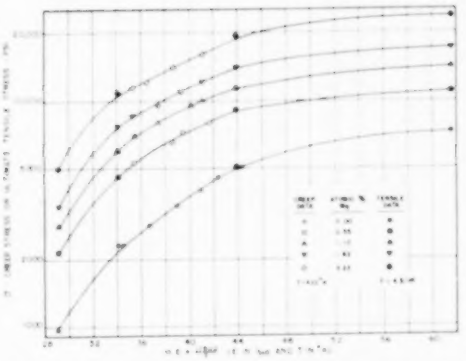

Fig. 1—Correlation of tension test data with creep data for Al-Mg solid solution alloys.

Materials, Equipment, Technique

In view of rather extensive correlatable data now available on the plastic properties of a series of binary α solid solutions of magnesium, copper, germanium, zinc, and silver in aluminum, these alloys were again selected for the present investigation. Previous reports have already covered the tensile properties of these alloys at subatmospheric temperatures,[3] and at elevated temperature,[4] as well as their fatigue properties at atmospheric temperatures,[5] and their creep properties at 422° K.[6] Resistivity measurements[7] as well as precision lattice constant determinations[8] revealed that these alloys are α solid solutions. After homogenization, 0.100 in. thick sheets were rolled to 0.070 in. in thickness and recrystallized to about the same grain size. Since the details of these treatments were reported previously,[6] they will not be repeated here. In order to appropriately reduce the scope of creep tests in this investigation only the typical alloys shown in Table I were investigated.

All creep specimens were machined such that their tensile axes were in the rolling direction of the 0.070 in. sheet stock. The gage section was 2 in. long and 0.500 in. wide with a reduced section of 3.50 in. Creep strains were measured by means of rack and pinion type extensometers with a sensitivity of 0.005 in. per division. Readings were estimated to 1/10 of

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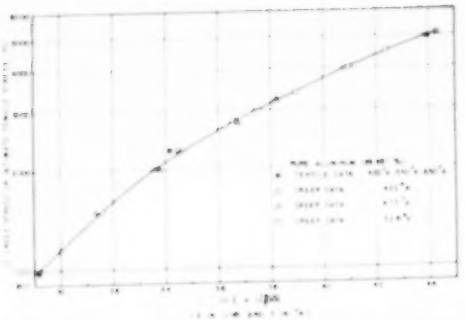

Fig. 2—Correlation of creep and tensile data of pure aluminum at various temperatures by the equation

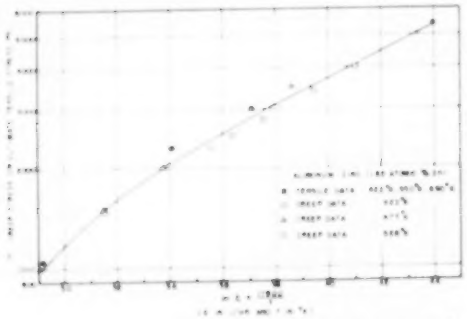

Fig. 3—Correlation of creep and tensile data of 1.62 atomic pct Zn in aluminum at various temperatures by the equation

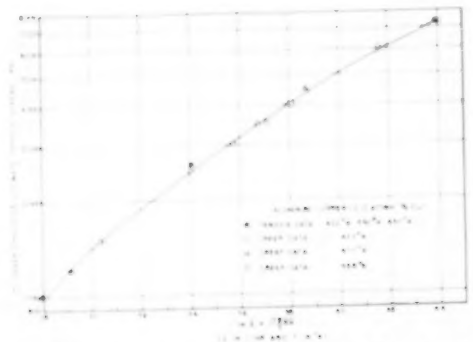

Fig. 4—Correlation of creep and tensile data of 0.10 atomic pct Cu in aluminum at various temperatures by the equation

a division; thus strains were detectable to approximately 0.00025.

Complete descriptions of the creep furnaces and equipment have been described in a previous report and will not be repeated here. Five creep temperatures were covered in the present investigation: 403 K (90 F), 373 K (212 F), 422 K (300 F), 477 K (400 F), and 528 K (491 F). Specimens were maintained at constant temperature within ± 1 K throughout the tests. All creep tests were performed under constant load conditions.

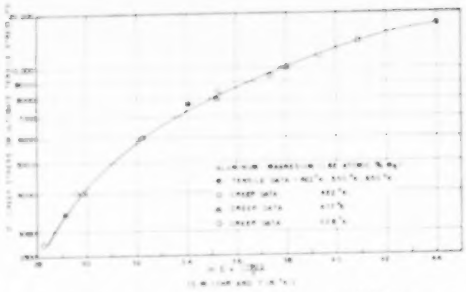

Fig. 5—Correlation of creep and tensile data of 1.62 atomic pct Mg in aluminum at various temperatures by the equation

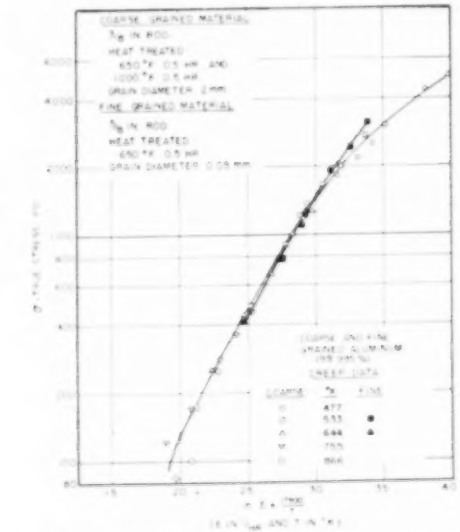

Fig. 6—Correlation of creep data of high purity aluminum at various temperatures by the equation Data of Servi and Grant.

Discussion of Results

The good correlation between the secondary creep data from 422° to 528 K and the ultimate tensile data from 422° to 650 K for the four alloys under investigation is shown in Figs. 2 to 5. The value of $\Delta H/R$ for each alloy was determined by noting that according to eq 1:

$$\dot{\varepsilon}_s e^{\Delta H/RT} = \dot{\varepsilon}_s e^{\Delta H/RT_s} = \text{(constant)}$$

for the same flow stress at two dissimilar creep test temperatures, T, and two corresponding secondary creep rates, $\dot{\varepsilon}$. Consequently:

$$\Delta H/R = \frac{\ln \dot{\varepsilon}_s/\dot{\varepsilon}}{\left(\frac{1}{T} - \frac{1}{T_s}\right)}$$

where $\dot{\varepsilon}_s$ is the secondary creep rate at T_s for the same flow stress that produces a secondary creep rate $\dot{\varepsilon}$ at temperature T.

A single activation energy of $\Delta H = 17{,}900\ R$ cal per mol was obtained for all of the alloys which

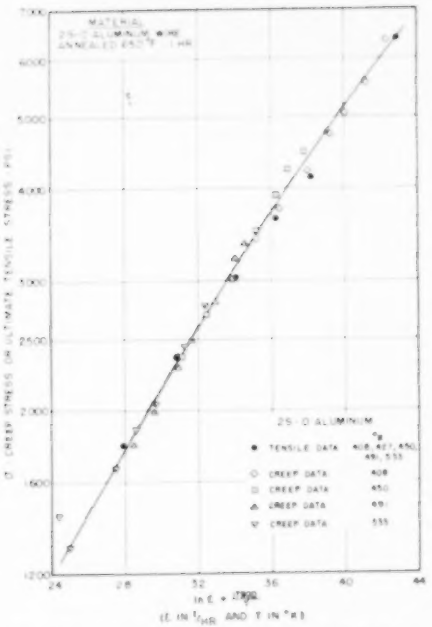

Fig. 7—Correlation of creep and tensile data of 2S-O at various temperatures by the equation $\sigma = \sigma_0 (\dot{\varepsilon} e^{17900/T})^{1/7}$. Data of Sinizer and MacGregor.[7]

were investigated over the range of secondary creep rates and temperatures referred to above. This favorable correlation between creep data and tensile data over wide ranges of temperature and strain rates suggests that the Zener-Hollomon parameter has rather broad utility for dilute α solid solutions. Evidently the metallurgical differences over the range of compositions studied here have little effect on the activation energy for creep.

Additional confirmation of the general utility of the Zener-Hollomon parameter for correlation of creep data is obtained by replotting Servi and Grant's[5] data for the creep of high purity aluminum for two different grain sizes as shown in Fig. 6. In this investigation the stress (and not the load) was held constant throughout each creep test; hence these data do not exactly parallel those given in Fig. 2 of this report where σ refers to the load per unit original area. Nevertheless these data also reveal that the activation energy for creep is $\Delta H = 17{,}900\ R$ cal per mol in complete harmony with the activation energies for creep of pure aluminum and the dilute binary α solid solutions of aluminum reported here. The same activation energy was obtained independent of grain size. Although the creep resistance of the fine grained aluminum is slightly superior to that of the coarse grained aluminum for values of $\ln \dot{\varepsilon} + 17{,}900/T$ greater than about 29.0, at lower values of this parameter the coarse grained aluminum exhibited superior creep resistance. The effect of grain size on the creep resistance, however, is quite small.

In view of the consistent appearance of an activation energy of $\Delta H = 17{,}900\ R$ for creep of high purity aluminum and its dilute alloys independent of grain size, it might be anticipated that 2S-O alloy, commercially pure aluminum, should also exhibit the same activation energy. Support for this contention is given by appropriate analysis of the data of Sinizer and MacGregor[7] on the creep of 2S-O alloy as shown in Fig. 7. Here the stress (as constant load per unit original cross-sectional area) is plotted as a function of $\ln \dot{\varepsilon} + 17{,}900/T$, where $\dot{\varepsilon}$ is the true secondary creep rate. The correlation of tension and creep data over wide ranges of temperature and true strain rates is remarkably good. But when a similar correlation was attempted for Servi and Grant's[5] data on 2S-O an activation energy of approximately 28,700 R cal per mol was obtained as revealed by the data given in Fig. 8. In view of the fact that the effect of grain size on the creep properties of high purity aluminum is very small, as shown in Fig. 6, and that the change in activation energy with grain size of high purity aluminum is not detectable, the large difference in activation energy for 2S-O between Sinizer and MacGregor's data and those of Servi and Grant is probably not ascribable to a difference in grain size. A possible source of this wide difference in activation energies for creep from two alternate samples of 2S-O alloy is revealed in the previously published data of Sherby and Dorn[6] on the effect of annealing on the creep properties of 2S-O alloy as shown in Fig. 9. These data reveal that the activation energy for creep increases with increased annealing temperature and that the increase in activation energy is inconsistent with the grain size trends as a comparison of the data in sections A and B of Fig. 9 reveals. A summary of the pertinent data available on 2S-O is given in Table II. These data unmistakably reveal that the activation energy for creep of 2S-O alloy is totally inconsistent with grain size but

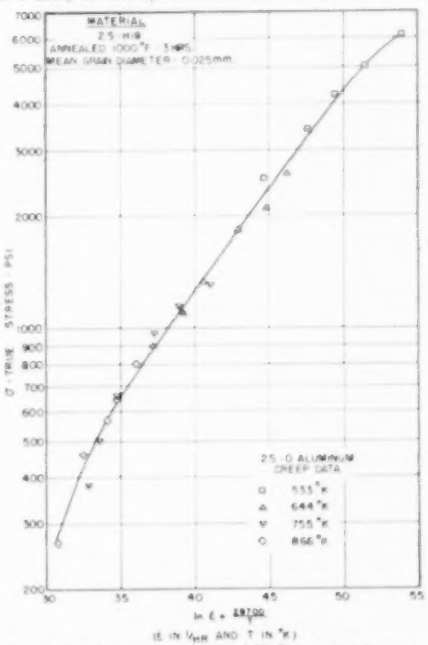

Fig. 8—Correlation of creep data of 2S-O at various temperatures by the equation $\sigma = \sigma_0 (\dot{\varepsilon} e^{17900/T})^{1/7}$. Data of Servi and Grant.[5]

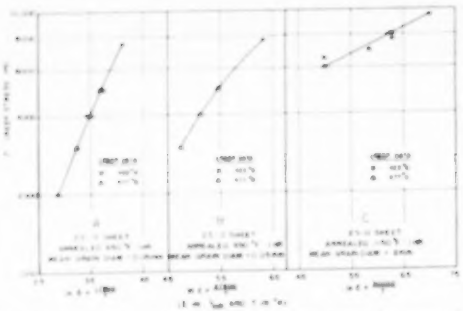

Fig. 9—Effect of annealing on the activation energy for creep of 2S-O alloy. Data of Sherby and Dorn.

that it increases in a regular way with the annealing treatment preceding creep testing. The basic cause for this effect has not yet been uncovered.

Range of Validity of Results

Since the creep stress σ is related to the secondary creep rate $\dot{\varepsilon}$ and temperature T by means of the single valued function

$$\sigma = \sigma(\dot{\varepsilon}e^{+Q/RT})$$

it must necessarily follow that the same metallurgical structure, representing the same state of the metal is obtained for all equal values $\dot{\varepsilon}e^{+Q/RT}$. Results on X-ray and metallographic examinations[7] of creep specimens of high purity aluminum and its alloys have shown that similar substructures are produced at equal values of $\dot{\varepsilon}e^{+Q/RT}$ for a given alloy. At high values of $\dot{\varepsilon}e^{+Q/RT}$ a very fine substructure is produced, whereas at lower values of $\dot{\varepsilon}e^{+Q/RT}$ coarser substructures result. The results of this investigation are mentioned here only to illustrate that identical substructures are produced at the same values of the Zener-Hollomon parameter at least for creep and tension data for pure aluminum and its dilute alloys at high temperatures.

The Zener-Hollomon parameter cannot be successfully applied at low temperatures. This is revealed by the data recorded in Fig. 10. Whereas the creep and tensile data over the range of 422° to 650°K, as shown in curve A, yield good correlation with $\ln \dot{\varepsilon} + \frac{17{,}900}{RT}$, the creep data at 373°K (curve B) and 305°K (curve C) do not correlate with this function. Correlation of the data over these temperatures could be achieved by assuming that the activation energy is a function of the temperature. This procedure, however, is theoretically unsound and does not lead to any practical utility. Consequently the correlation of creep and tensile data for aluminum and its dilute alloys can be obtained only for temperatures in excess of about 400°K at which recovery becomes active. Apparently, at lower temperatures the more complex phenomena associated with strain hardening enter and prohibit the unmodified application of the Zener-Hollomon concept.

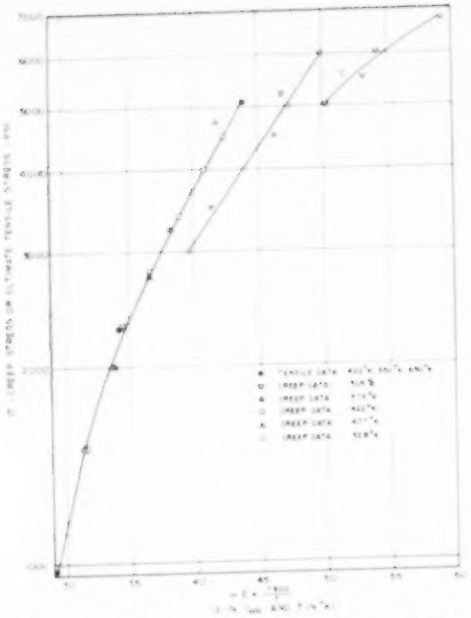

Fig. 10—Correlation of creep and tensile data of pure aluminum at various temperatures by the equation $\sigma = \sigma(\dot{\varepsilon}e^{+Q/RT})$.

This discussion reveals that over appropriate ranges of secondary creep rates and temperatures, the activation energy for creep of aluminum and its dilute α solid solution alloys is 17,900 R cal per mol independent of grain size, alloy or composition, and structure. Such facts suggest that the activation energy for these materials is 17,900 R cal per mol not only during the secondary stage of creep but also during the primary or transient stage of creep where structural changes are occurring due to simultaneous effects of deformation and recovery.

If this is true, a temperature compensated time:

$$\theta = te^{+Q/RT}$$

where t is the time under stress, should permit correlation of the total creep curve of creep strain vs. θ for any given stress over wide ranges of creep temperatures. Inasmuch as the activation energy for creep of aluminum and its dilute alloys is 17,900 R cal per mol, the expected correlation of the total creep curve for a single stress should be obtained by plotting the creep strain as a function of:

$$\theta = te^{+17{,}900/RT}$$

The verification of this concept is illustrated in Figs. 11 and 12. This method of correlation of complete creep curves is shown to be excellent for the data for the aluminum alloy containing 0.101 atomic pct Cu

Table II. Effect of Annealing on the Activation Energy for Creep of 2S-O Alloy

Investigator	Original Stock	Annealing Treatment	Mean Grain Diameter, mm	Activation Energy, cal per Mol
Sherby and MacKenzie	2S-O wire	650°F for 1 hr	0.05	17,900 R
Sherby and Dorn	2S-O sheet	650°F for 1 hr	0.05	17,900 R
Sherby and Dorn	2S-O sheet	900°F for 1 hr	0.05	27,500 R
Sherby and Dorn	2S-O sheet	1000°F for 3 hr	0.025	28,700 R
Sherby and Dorn	2S-H18 bar stock	1130°F for 1 hr	2.0	30,000 R
Servi and Grant	2S-O sheet			

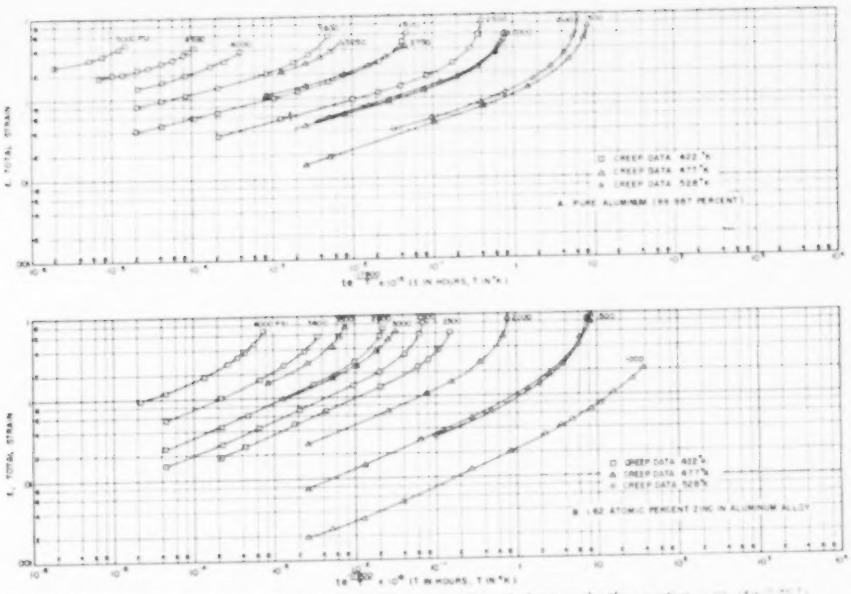

Fig. 11—Correlation of creep strain-time data of α solid solution alloys of aluminum by the equation $\epsilon = f(t\theta^{-n})$.

as shown in Fig. 12A. Exact agreement is obtained when the creep strain at a stress of 1500 psi is plotted as a function of θ for creep temperatures of 477° and 528°K. At a creep stress of 3500 psi agreement is again achieved in the ϵ–θ curves for creep at 422° and 477°K. Furthermore all of the creep curves for the Al-Cu alloy shown in Fig. 12A give a uniform and consistent family of curves of ϵ vs. θ for all stresses and temperatures which were investigated. Good correlations were also obtained for the high purity aluminum (Fig. 11A) and the aluminum alloy containing 1.62 atomic pct Mg (Fig. 12B). The data for the alloy containing 1.6 atomic pct Zn exhibit slight random deviations from exact correlations. These

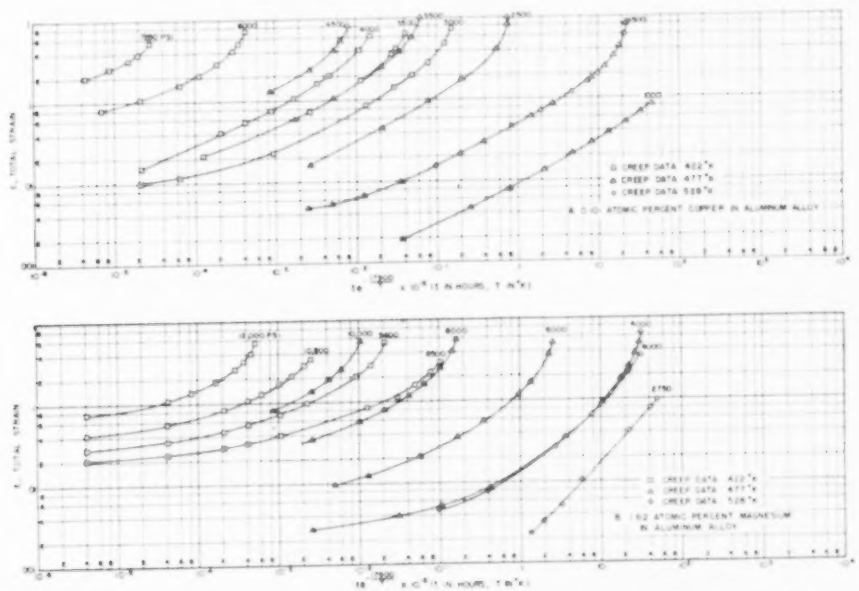

Fig. 12—Correlation of creep strain-time data of α solid solution alloys of aluminum by the equation $\epsilon = f(t\theta^{-n})$.

minor inconsistencies in the data for the Al–Zn alloy however, were noticeable in earlier investigations and might be attributable to variations in sampling rather than failure of the concept of a temperature compensated time for correlation of creep curves. In general, these data reveal that the activation energy for creep is the same throughout the primary as well as the secondary stage and thus the activation energy for creep is independent not only of the various substructures developed during secondary creep under different conditions of temperature and stress, but it is also independent of the changes in structure due to deformation and recovery during the primary stage of creep.

A major problem in the application of creep data to engineering design concerns the necessity of extrapolating short time creep tests of 10^2 to 10×10^2 hr to service lives of as much as 250×10^2 hr. No safe method for this extrapolation has yet been uncovered because no suitable method for predicting the time of onset of the tertiary stage of creep is known. This deficiency in ability to predict the beginning of the tertiary stage of creep might easily be circumvented by a simple procedure involving the use of the temperature compensated time, $\theta = te^{-\Delta H/RT}$. For example, if the complete creep curve is desired for a design stress of σ, and a temperature T_1, an incomplete short time creep test up to say 10^2 hr might be obtained. A second test at the same stress σ, and temperature T_2 where $T_2 > T_1$ might be run where T_2 is so selected that a complete creep curve to rupture is obtained in less than 10^2 hr. Then

$$t_1 e^{-\Delta H/RT_1} = t_2 e^{-\Delta H/RT_2}$$

where t_1 and t_2 are the times for test one and test two to reach the same strains. Hence ΔH can be evaluated and now both tests can be plotted as ϵ vs. θ. Thus the total strain ϵ at time t for the selected stress σ, and the temperature T_1 can be deduced from the composite data of ϵ vs. θ. Furthermore, this composite creep curve also represents the creep curve at any other temperature T for the stress σ. In this way much of the doubt concerning extrapolation of creep data to long times can be eliminated. Of course, this analysis was found valid for simple alloy systems. Perhaps these elementary methods of analysis are not generally applicable to complex engineering alloys in which major structural changes occur during the time interval at the creep temperature. Undoubtedly more thorough investigations will have to be made on the general validity of the temperature compensated time concept before its unqualified acceptance for extrapolation of short time creep tests is assured. At present this possibility appears interesting and useful.

Conclusions

1—Creep and tensile data of a solid solution alloys of aluminum above 400° K can be simply related by the Zener-Hollomon relation $\sigma = \sigma_0 (Ze^{-\Delta H/RT})$ where ΔH was found to be 35,800 cal per mol for all the alloys investigated. Such correlations were thought to arise from the fact that the structural changes occurring during deformation at these temperatures are simple functions of the strain rate and temperature.

2—The Zener-Hollomon parameter alone was not adequate for correlating creep and tensile data at temperatures below about 400° K for aluminum.

3—Tensile and creep data on 2S-O by various investigators were also correlated by the Zener-Hollomon parameter. The activation energies obtained, however, differed from one series of data to another, dependent upon the annealing conditions preceding creep.

4—When creep strains for a stated creep stress are plotted in terms of a temperature compensated time, $\theta = te^{-\Delta H/RT}$, a single creep curve is obtained independent of the creep temperature. This suggests a simple method for extrapolation of short time creep data to much longer times.

Acknowledgments

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Some Observations of Subgrain Formation During Creep In High Purity Aluminum

by Italo S. Servi, John T. Norton, and Nicholas J. Grant

Coarse grained high purity aluminum was tested in creep at temperatures of 400° to 1200°F to develop subgrain structures. Measurements of subgrain size, distribution, and rotation were made from X-ray diffraction patterns. Subgrain size and distribution were checked metallographically and the size was compared with average slip band spacing. The slip family was determined for several specimens.

THE interest and research recently evident abroad in the role of subgrain formation and polygonization as a contribution to the creep of metals at elevated temperatures is deserving of greater attention in this country. Such metallic subgrains can be defined as macroblocks existing within the grains. The general observation has been that the macroblocks which belong to the same grain have a maximum difference in orientation of a few degrees. In spite of the considerable amount of work that has been done since Jenkins and Mellor[1] observed the "division of existing crystals into smaller units when deformation occurs at an annealing temperature," the subject of subgrain formation is only now receiving truly active discussion and investigation.

The existence of subgrains has been revealed by metallographic methods, as in the work of Jenkins and Mellor,[1] and by X-ray methods, first applied to this problem by Homes.[2] Hirst[3] and Calnan and Burns[4] applied the back-reflection Laue technique to the study of coarse grained specimens. Wood et al.[5] and Greenough and Smith[6] examined the ring obtained with a back-reflection camera for the study of fine grained specimens. In addition to the above, the transmission technique was used by Wood.[7] A special technique was developed by Guinier and Tennevin[8] in order to improve the resolution.

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Metallographically, the subgrains have been observed directly on the surface of deformed specimens by Wood et al.,[5] or have been made evident on repolished surfaces by applying a suitable etching reagent. The latter technique, first suggested by Lacombe and Beaujard,[9] was then improved by Wyon and Crussard.[10]

Subgrains can be formed in single crystals after small amounts of bending followed by heating after this cold work, or during deformation at elevated temperatures. The first phenomenon was analyzed by Cahn[11] for the simple case of pure bending followed by annealing. Cahn suggested a mechanism of subgrain formation based on the dislocation theory and called this phenomenon "polygonization." He extended this mechanism to the more complex case of local bending, such as the bending which may occur when a polycrystalline specimen is deformed in tension. Cahn's suggestion was later found quite consistent with the results obtained by Dunn and Daniels.[12]

An explanation has been presented recently regarding the formation of subgrains during deformation at elevated temperatures by Chang and Grant.[13] In general, there are two schools of thought on the subject. One, according to Wood et al.,[5] is that subgrain formation is a mechanism of deformation which is operative under certain conditions in the same way that the slip process is the mechanism of deformation which is operative under other conditions. The boundaries between the subgrains undergo a viscous flow which contributes substantially to the deformation of the material. The second, according to Cahn,[11] Wyon and Crussard,[10] and Chang and Grant,[13] is that subgrain formation is the effect of simultaneous deformation and annealing and is,

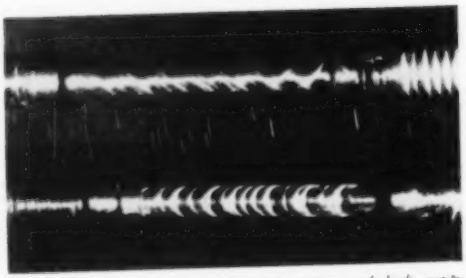

Fig. 1—Two views of a single crystal specimen of high purity aluminum deformed at 1200 F at an initial stress of 70 psi. X15.

therefore, a special case of polygonization. The subgrain formation is especially associated with the deformation bands along which the crystals undergo progressive bending. Subgrain formation is a recovery-type process and, therefore, does not involve nucleation.

The present investigation has been undertaken to study some of the aspects of formation of subgrains during creep of high purity aluminum. The metallographic and X-ray observations will be compared with the structural observations made by Servi and Grant[7] on the same high purity aluminum deformed in creep.

Experimental Procedure

The material used was high purity aluminum, furnished by the Aluminum Co. of America, specified as 99.995 pct Al. The reported spectrographic analysis of the impurities was: Cu, 0.0017 pct; Fe, 0.002; Si, 0.001; Mg, 0.0002; Na and Ca, 0.0006.

The specimens consisted of cylindrical tensile specimens of 0.16 in. diam and 1 in. gage length. Some of the samples (coarse grained) were annealed at 1000 F to a grain size of 1 to 3 mm. Other samples, consisting of one to three grains in the gage section (special) were prepared by the strain-annealed method. The final annealing temperature in this case was 1180 F. Several samples chosen at random from both lots were examined by X-ray diffraction before testing with no indication of a subgrain structure.

All the samples were electropolished before testing. The coarse grained samples were tested in creep at constant stress in the temperature range 400° to 1100 F. The special specimens were tested at constant load at 1000°, 1100°, and 1200 F. In all cases the reduction of area in the parts of the specimens which were examined was of the same order of magnitude, about 10 pct.

The following metallographic techniques were applied to the study of the deformed samples:

1—Direct observation with no further preparation.

2—Electrolytic repolish and etching with the Lacombe and Beaujard reagent.[8] Etch pits are formed preferentially along subgrain boundaries.

3—Electrolytic repolishing in 35 pct hydrochloric acid at an open circuit voltage of 50 v. The subgrain boundaries are attacked heavily.

4—Repolishing in the acetic acid-perchloric acid mixture[9] at 40°C. Blisters are formed along the subgrain boundaries.

The X-ray technique employed a Laue back-reflection camera using a copper tube energized at a voltage of 45 kv. The specimen to film distance was 3 cm. The beam had a diameter of 1 mm at the point of incidence. Patterns were obtained both from the surface and from the inner part of deformed specimens which had been longitudinally sectioned.

The method of determining the average size of the subgrains from the X-ray patterns is of necessity an approximate one and while the number obtained will obviously be too small, the relative values should be correct. Knowing the size of the incident X-ray beam and making an assumption about the depth of penetration, the volume of metal contributing to a particular reflection is calculated. Again assuming that each subgrain in this volume will give a reflection lying in the patch of subgrain spots, these spots are counted and in this way the average size of the subgrains is computed. Small subgrains may give spots too weak to be recorded and others may overlap, so that the number counted will be smaller than the true value. However, if conditions of exposure are kept constant, the relative values of the subgrain size obtained in such a manner should be significant in indicating the influence of such variables as stress or temperature.

Experimental Results

It is unfortunate that all the results obtained from about 150 X-ray diffraction patterns and 100 micro-

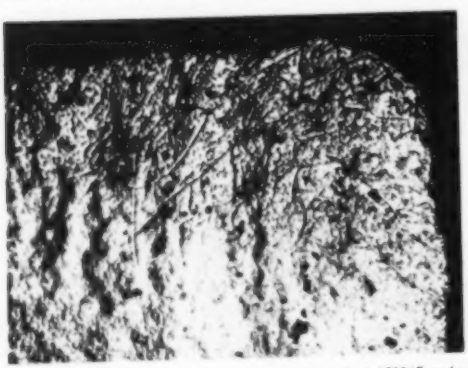

Fig. 2—Transverse section of a specimen deformed at 1200 F under 40 psi showing subgrain boundaries. Polished in concentrated hydrochloric acid. X50. Area reduced approximately 20 pct for reproduction.

Fig. 3—Special specimen deformed at 1200 F at 70 psi showing subgrain boundaries. Repolished in modified Jacquet's reagent at 40 C. X150. Area reduced approximately 20 pct for reproduction.

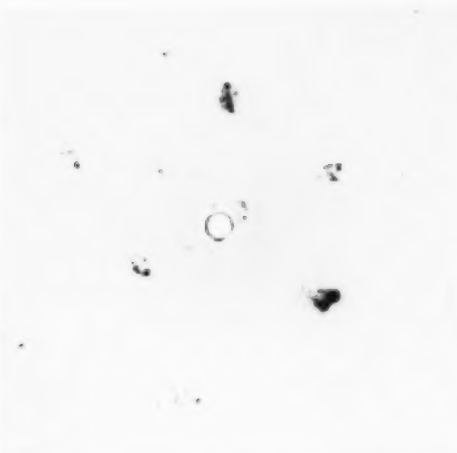

Fig. 4—X ray back reflection pattern of a coarse grained specimen deformed at 900° F at 190 psi. Beam approximately parallel to the main slip planes and perpendicular to the axis of the specimen.

Fig. 5—X ray back reflection pattern of a coarse grained specimen deformed at 900° F at 450 psi. Beam perpendicular to the axis of the specimen.

graphs cannot be reported in detail. Instead the results shall be summarized and a few typical photographs will be presented. Fifteen coarse grained and six special specimens were tested in creep and examined. In all cases the examined sections of the specimens which were studied showed well-developed slip bands. A typical example is presented in Fig. 1, which shows the photograph of a single-crystal specimen deformed at 1200° F at an initial stress of 70 psi.

The approximate determination of crystal orientation revealed that the slip plane may belong to one of the following families: (111), (100), or (211). The angle of the active slip plane (as measured by the normal to this plane) relative to the stress axis was always between 40° and 50°. In all cases the slip direction belonged to the [110] family. This [110] slip direction was at an angle of 40° to 50° from the stress axis. These results differ from the previous observations[7] concerning the active slip system operative at low temperature [(111), [110]], and the active slip system [(100), [110]] operative at high temperatures. The slip plane was determined by the Laue back-reflection technique. The specimen was set in a holder in such a way that the slip plane was perpendicular to the X-ray beam. When the slip process was well underway (see Fig. 1, for example), the slip direction was easily noted; as a consequence, its orientation with respect to the film was known. Later, by the use of the Greninger chart,

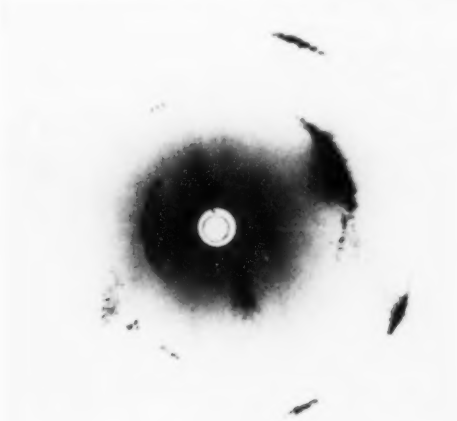

Fig. 6—X ray back reflection pattern of a coarse grained specimen deformed at 500° F at 1300 psi. Beam perpendicular to the axis of the specimen. Diffraction rings due to the strong characteristic wavelength are observed in this pattern.

Fig. 7—X ray back reflection pattern of a coarse grained specimen deformed at 500° F at 2000 psi. Beam perpendicular to the axis of the specimen.

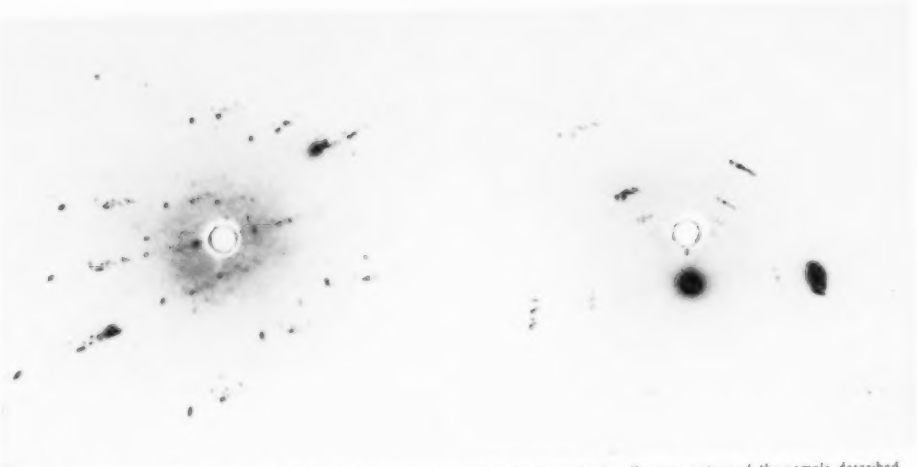

Fig. 8—X ray back reflection pattern of a special specimen deformed at 1200° F at 70 psi. Beam perpendicular to the axis of the specimen and approximately perpendicular to the axis of rotation.

Fig. 9—X ray back reflection pattern of the sample described in Fig. 8. Beam perpendicular to the axis of the specimen and approximately parallel to the axis of rotation.

the slip plane and slip direction were established.

The observation of subgrains by metallographic methods is restricted to subgrains having a rather coarse size. The direct observation of the surface of deformed samples did not reveal subgrains except in a few cases which were reported previously.[3] The etch-pit method was successful but gave rather confused results in some samples. Electrolytic polishing in concentrated hydrochloric acid for less than 1 min etched the subgrain boundaries deeply as shown in polishing Fig. 2. The substructure is reproducible after light polishing and re-etching. The background by such a technique is always rough and therefore many details are missed. Repolishing in acetic-perchloric acid mixture[7] at 40° C was the most suitable method to reveal the subgrains. However, at the present stage of the investigation, this technique is not easily controlled although the reproducibility was good in many cases. The subgrain boundaries are outlined by small round blisters which are also scattered at random inside the subgrains (see Fig. 3).

The metallographic observations indicated that the size of the subgrains could be very irregular. The determination of the average subgrain size was, therefore, only approximate. Since the grain boundaries are barriers for the subgrain boundaries, the substructures of two adjacent grains may be independent of one another and are dependent only on the deformation occurring in each grain.

When a specimen forms subgrains, the X-ray Laue spots are broken up into several elements of different intensity which may partially overlap. Whenever the orientation of some subgrains is such that the strong characteristic wave lengths can be reflected, a portion of a spotty ring is visible in the back-reflection Laue picture. Such Debye reflections shall be disregarded and only the reflections due to the white radiation shall be studied.

Each patch of subgrain spots represents the re-

Fig. 10—Stereographic projection obtained from the X ray pattern of Fig. 8.

Fig. 11—Stereographic projection obtained from Fig. 9. This projection can be obtained from Fig. 10 by rotating the poles 83° about the axis of the specimen.

flection of one crystallographic plane. It was observed that the number of spots existing in each patch is larger the higher the applied stress. The angular spread also increases, but more irregularly, as the stress increases. Figs. 4 to 7 reveal the effect of the stress. Other X-ray patterns indicated that the same subgrain structure was found for samples deformed at 1000 psi at 400°, 500°, and 700° F, respectively. Fig. 7 indicates that at 2000 psi the subgrain size approaches the limits of resolution of the technique used; specimens deformed at 3000 psi or more gave rise to diffuse reflections. The largest angular spread observed was about 15°.

Although in no case are the subgrain spots located in patterns corresponding to simple rotation, at least in the simplest cases the distribution of the subgrain spots corresponds as a first approximation to a rotation about an axis which lies in the slip plane and is perpendicular to the slip direction. Such a fact is not always evident if the orientation of the X-ray beam relative to the slip system is chosen at random as in the cases of Figs. 4 to 7. However, the rotation can be determined when the X-ray beam is approximately perpendicular or parallel to the axis of rotation. In the first case, see Fig. 8, the subgrain spots are distributed along hyperbolas; in the second case, see Fig. 9, the spots are distributed along circles. The stereographic projections of the two cases have been presented in Figs. 10 and 11, respectively. In the case of the specimen investigated, the active slip system was the [1211], [110]] the axis of rotation was the [111]. This fact is clearly shown in Fig. 9 in a way which is completely independent of the accuracy of single-crystal determination.

Although Figs. 8 and 9 represent almost ideal cases of simple rotation, it is evident that many spots do not lie along hyperbolas and circles. It was observed that the break-down approaches the case of simple rotation only when well-developed and regular slip bands belonging to a single slip system are present. Smaller grains, which have less freedom of deformation and therefore undergo a more complex type of deformation, gave origin to less regular patterns.

In order to determine whether the break-down of grains is a surface phenomenon or not, some samples were cut and repolished. There was no marked difference between the appearance of an X-ray pattern taken on the surface and the appearance of a pattern taken on a cut section, provided that the orientation of the X-ray relative to the crystal was the same in both cases.

Furthermore, Gervais,[7] using an etch composed of HCl, HF, and HNO_3 in alcohol revealed a subgrain structure which is retained as metal is removed from the surface. The change in size of the individual subgrains can be followed easily in Fig. 12; about 0.001 in. of metal has been removed between repolishing and etching steps.

A comparison of X-ray patterns obtained from different parts of the same crystal after severe deformation (specimen was fractured) revealed within the limits of the sensitivity of this method no substantial difference in subgrain size between the region crossed by a slip band, and the region between two slip bands. On the other hand, much larger differences were noted at points near grain boundaries as compared to centers of grains.

A summary of the results, including the measurements of slip band spacing, and the measurements of subgrain size as determined by X-ray and metallographic methods are reported in Tables I and II. The values reported in each line are the corresponding values obtained for one chosen grain of each specimen. With this in mind, the results can be compared with more extensive data obtained by Servi and Grant[3] for the average slip band spacing of the same high purity aluminum as a function of the applied stress, and with Orowan's theory[10, 11] of minimum slip band spacing as a function of the stress.

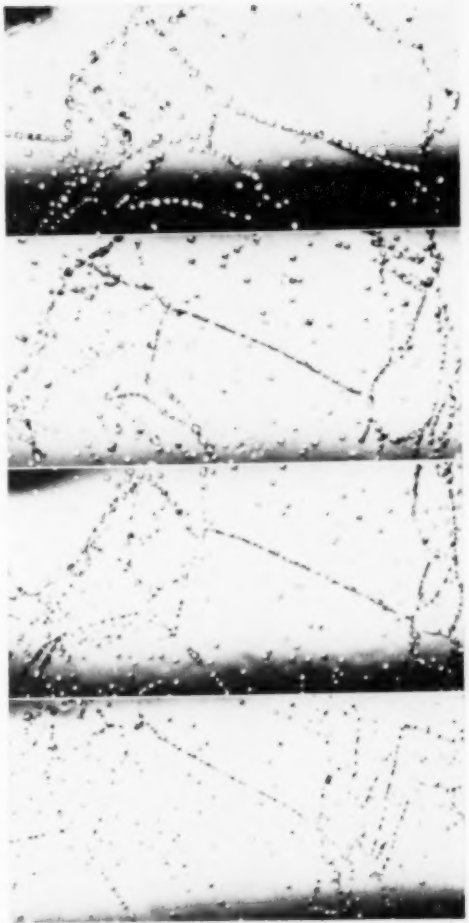

Fig. 12—Gradual change in substructure as 0.001 in. of metal is removed from surface after each repolish and etch. HCl, HF, and HNO_3 in alcohol. X100. Area reduced approximately 20 pct for reproduction.

The data of Tables I and II indicate that both the average slip band spacing and the subgrain size increase as the applied stress decreases.

Discussion

The X-ray back-reflection Laue technique applied to single crystals or coarse polycrystalline specimens deformed in creep is suitable to investigate the presence of subgrains, although not in a quantitative way in a 3 cm camera. The results should be compared with metallographic observations whenever possible. The orientation of the X-ray beam relative

Table I. Values of Subgrains, Slip Band Spacing, and Slip Family for Coarse Grained High Purity Aluminum Deformed in Creep at Elevated Temperatures

			X-ray Back Reflection						
Specimen No.	Stress, Psi	Temperature, °F	No. Sub-Grain Spots	Maximum Angular Spread, Deg	Average Size Subgrains, Mm	Average Slip Band Spacing, Mm	Slip Plane (Family)	Slip Direction (Family)	Axis of Rotation (Family)
104	Tensile test	Room	Diffuse spots	15					
35	5000	400	Diffuse spots	14		0.600			
40	3000	500	Diffuse spots	12		0.607			
62	2000	500	1000	10	0.031	0.032			
41	1000	400	1000	12	0.031	0.03			
28	1200	500	700	10	0.035	0.034			
66	1150	450	500	13	0.045	0.02			
23	1000	500	500	10	0.045	0.025			
24	900	500	500	15	0.045	0.02			
31	900	500	40	10	0.14	0.15	(100)	(110)	(110)
30	700	500	40	10	0.08	0.02			
27	450	500	150	10	0.08	0.02			
43	400	500	70	8	0.12	0.1			
45	400	500	70	8	0.2	0.3			
26	170	1100	25	5	0.2	0.5			
42	150	1000	30	8	0.18	0.5			
82	100	1100	25	6	0.2	0.7	(211)	(110)	(111)

to the crystal is of the greatest importance in order to obtain the best information and to interpret the results adequately.

The fact that several slip systems have been observed indicates that at elevated temperatures the resolved critical shear stress is similar along several planes. That system, therefore, which is more favorably oriented, becomes active.

The deformation process at elevated temperatures is essentially a process of crystallographic slip, but due to the existence of many potential slip systems and the complication of structure in polycrystalline specimens, some degree of bending is always to be expected.

The formation of subgrains is indirectly related to the slip process in the grain. The rotation of the subgrain spots is not a mere consequence of the "local curvature" of the crystal lattice near the glide planes because no peculiar subgrain distribution was observed near the slip planes. More probably the subgrain formation is a polygonization process due to local bending and simultaneous annealing. The local bending may be originated by the formation of deformation bands, since the axis of rotation of the deformation bands[7] coincides with the axis of rotation of the broken-up spots.

A sample deformed in tensile creep develops slip bands and deformation bands which are highly irregular. Hence, even the formation of subgrains must be irregular, as was observed. This is the reason for the striking difference in regularity between an annealed metallic structure and a substructure. The state of equilibrium which is reached during creep testing, as far as the substructure is concerned, is not based on a state of minimum surface energy, but on a state of minimum strain energy. This hypothesis agrees with the mechanism of polygonization[7] according to which a state of minimum energy is reached when the existing dislocations are distributed along certain patterns. Such a pattern can be predicted for the case of simple bending of single crystals followed by annealing.[7] However, since in the case of polycrystalline specimens deformed in tensile creep the state of local bending is not known, the final substructure cannot be predicted.

The results of the present investigation revealed that, even at the highest temperatures, the slip process is directly responsible for the deformation of single crystals. In no instance did single-crystal specimens reveal subgrain boundaries on the "as-deformed" surface, indicating that no appreciable flow occurred along the subgrain boundaries. The observation of crystalline slip can be extended to the case of coarse grained polycrystalline specimens which revealed, in addition, flow occurring along the grain boundaries to a very appreciable extent.

At the present stage of this investigation the observation that the average size of the subgrains is inversely proportional to the applied stress is only roughly quantitative. There is a clear indication that for a constant amount of deformation and a constant stress level the number of subgrain spots forming the X-ray reflection of a single crystallographic plane, and the angular range of orientation of these spots do not depend markedly on the temperature. There is also evidence that the average size of the subgrains, as determined by counting the subgrain spots, is somewhere between one and four times smaller than the average slip band spacing. Wherever direct comparison is possible, metallographic observation gives much smaller values of subgrain size, but it should be remembered that in the X-ray pattern of subgrain spots some are too

Table II. Comparison of X-ray and Metallographic Values of Subgrain Size in Coarse Grained Aluminum Tested in Creep at Elevated Temperatures

			X-ray Back Reflection								
Specimen No.	Stress, Psi	Temperature, °F	No. Subgrain Spots	Maximum Angular Spread, Deg	Average Size Subgrains, Mm	Average Slip Band Spacing, Mm	Subgrain Average Size from Metallographic Methods, Mm	Ratio of Slip Band Spacing to Average Subgrain Size, Metallographic	Slip Plane (Family)	Slip Direction (Family)	Axis of Rotation (Family)
5	100	1000	33	6	0.28	0.8			(100)	(110)	(110)
9	50	1100	25	4	0.28	2.0			(111)	(110)	(111)
120	40	1200	4	3	0.5	2.0	0.07	30	(111)	(110)	(211)
102	35	1200	5	2	0.4	1.2	0.02	60	(111)	(110)	(111)
91	70	1200	10	9	0.28	0.8	0.01	80	(211)	(110)	(111)
121	70	1200	10	8	0.31	1.6			(111)	(110)	(211)

weak to record and others overlap, so that the X-ray method gives too high a value for average size. It must be concluded, therefore, that from metallographic observations of these specimens the subgrain diameter on the average is smaller by at least a factor of 30 than the average slip band spacing. If more weight is given to the rather limited information obtained from the metallographic observations, see Table II, it can be concluded that the average size of the subgrains approaches the theoretical value for minimum slip band spacing predicted by Orowan.[31]

As the applied stress increases, the size of the subgrains decreases as indicated by the increase in the number of subgrain spots in each X-ray reflection; and, for very high stress, as in the case of room temperature tensile testing, the subgrain spots merge into smooth diffuse reflection spots. This result suggests that there is no sharp transition between the high stress and the low stress mode of deformation of the metallic grains, the difference being only a matter of size of the subgrains. In actual creep testing, high stress is generally associated with low temperature, and low stress with high temperature. There is no difference between the mode of high temperature and the low temperature deformation of the metallic grains. The markedly different behavior observed in polycrystalline specimens tested at low temperatures and at high temperatures[32] has its origin in the deformation occurring at the grain boundaries.

Summary

1—Creep testing of coarse grained and single-crystal specimens of high purity aluminum was performed from 400° to 1200°F. The deformed specimens were examined by metallographic methods and by an X-ray back-reflection Laue technique.

2—In all cases slip bands were observed. The slip systems were: [(111), [110]] [(100), [110]], or [(211), [110]].

3—The metallographic and X-ray techniques revealed the presence of subgrains both on the surface and inside the deformed specimens. The subgrains are larger the lower the applied stress.

4—The average size of the subgrains is smaller than the average slip band spacing and approaches the value predicted by Orowan's theory for the minimum slip band spacing (based on metallographic determinations).

5—The orientation of a family of subgrains belonging to the same grain corresponds, as a first approximation, to a rotation about an axis lying in the slip plane and perpendicular to the slip direction.

6—The results suggest that the slip process is the primary mechanism of deformation of the metallic grains even at elevated temperatures, when the grain size is large enough to permit slip to be operative. This is a confirmation of the earlier results of Servi and Grant.[33,34] Subgrain formation is not the primary mechanism of deformation of the grains at elevated temperatures. These subgrains form by a polygonization process due to local bending caused by nonhomogeneous grain boundary sliding and concurrent annealing. The well-known difference in the overall high and low temperature behavior of polycrystalline specimens is, therefore, based on the behavior of the grain boundaries and not of the grains.

Acknowledgments

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Recrystallization Kinetics of Low Carbon Steel

By Stanley F. Reiter

The paper presents isothermal recrystallization curves for 0.08 and 0.15 pct C steel at subcritical temperatures following small amounts of plastic deformation. The effects of deformation, temperature, and aging on nucleation and growth rates are described. The free energy of activation for grain boundary migration in steel is given.

SEVERAL excellent reviews of the literature have appeared concerning the recrystallization of metals.[1-3] The present investigation follows the approach advanced by Mehl, Stanley, and Anderson,[4] in which the rate of recrystallization was analyzed in terms of N, the rate of nucleation, and G, the rate of growth of recrystallization nuclei.

Two lots of low carbon, capped steel of the analysis given in Table I were studied. Each lot consisted of a 150 lb coil which had been hot rolled to 0.083 in. and then cold rolled to 0.042 in. at the mill. Strips 0.930 in. wide were sheared perpendicular to the rolling direction.

Both steels were normalized before studying their recrystallization characteristics. The strips were cleaned, painted with a magnesia-acetone paste, and made into packs of equal weight, wrapped in 0.002 in. copper foil. The packs were placed in a salt bath at 900°C for 30 min and air cooled. A relief anneal followed in a second salt bath for 15 min at 650°C.

The relief anneal was found necessary from early tests in which a longer incubation period and slower rate of recrystallization were observed in relief-annealed lot A steel than in similar material which was strained and recrystallized directly after being normalized. This effect, which indicates the presence of transformation and/or cooling stresses in steel air cooled from above the A_1 temperature, has also been observed by Samuels[5] and Masing.[6] Figs. 1 and 2 show the microstructure of lot A and B materials and illustrate the rather uniform No. 8 ASTM grain size produced by this heat treatment.

Winlock and Leiter[7] observed that strip specimens which had their sharp edges removed elongated more uniformly than those which were not polished. Similarly, when the sheared edges were removed on a belt grinder, it was found in the present investigation that such samples recrystallized more uniformly than did unpolished strips. Therefore, all strips were carefully rounded prior to their extension.

The approximate strain limits for the production of large recrystallized grains are from 6 to 12 pct extension.[8] It was found that for the purpose of this investigation, 8 and 9 pct elongation were suitable deformations. The strain rate employed was 0.01 in. per in. per min and produced a yield point elongation of 4 pct. Winlock and Leiter found that mild steel of No. 8 ASTM grain size gave the same yield point elongation when extended at 0.012 in. per in. per min.

All of the lot A and B strips extended in tension developed a straight, stretcher strain line at each grip when the upper yield point was reached. The lines were parallel and made an angle of 55° with the edge of the strip. They approached each other with increasing strain and met near the center of the sample at the end of the yield point elongation. Immediately thereafter, a small drop in load was observed and then the load increased in a regular manner with increasing extension.

The grips were initially 8 in. apart. After extension, the 6 in. gage length was carefully cut into 1 in. samples. The remainder of the strip was discarded. After a flash pickle in hot 50-50 hydrochloric acid, six samples, each of which had been taken from a different strip, were placed in a basket and submerged in a lead pot for isothermal recrystallization. Although no recovery effect was observed, strain aging did occur after extension. Therefore, samples were always recrystallized within 24 hr after their cold deformation.

After recrystallization, the samples were etched with a solution comprised of one part by volume of nitric acid with three parts of water. Bromide printing paper was exposed directly at low magnifications and later used with a mask to measure the desired quantities. First, the average diameter of the largest grain visible in each sample was determined using dividers. Next, the number of recrystallized grains per unit area was counted and recorded as n. Then, for each sample, the combined area of the recrystallized grains was measured by transcribing the grain outlines to standard graph paper. Many determinations of the area of the recrystallized grains were repeated five times and indicated a standard error that was not greater than ±5 pct. The average area for six samples was divided by the area of the mask to yield the percentage recrystallized.

Recrystallization of 0.08 Pct C Steel

The progress of recrystallization at 670°C after 8 pct elongation of lot A steel is shown in Fig. 3, a through f. The shapes of the growing crystals are approximately equiaxed, as is assumed in the

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This paper represents part of a thesis by S. F. Reiter submitted in partial fulfillment of requirements for the degree of Doctor of Engineering to the Graduate School of Engineering, Yale University.

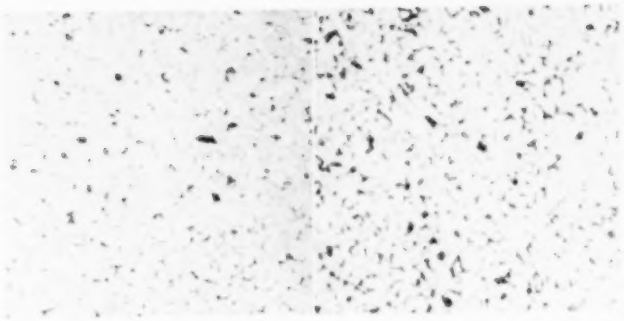


Fig. 1—0.08 pct C steel normalized and relief annealed. X100.

Fig. 2—0.15 pct C steel normalized and relief annealed. X100.

mathematical analysis of two-dimensional recrystallization.[7] The scalloped, irregular boundaries indicate that G has been influenced by at least three factors: 1—the obstruction offered by carbide particles, 2—the difference of orientation between the growing crystal and the cold worked grain being consumed, and 3—the heterogeneity of the strain pattern within the cold worked grains, Figs. 19 and 20.

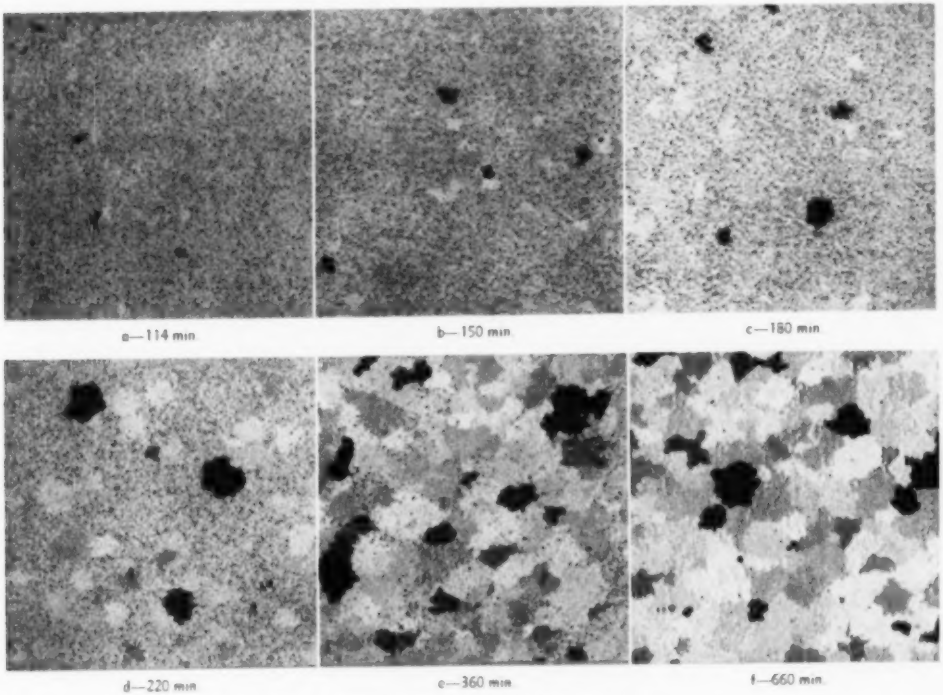
Effect of Temperature and Deformation

Fig. 4 shows the isothermal recrystallization curves obtained for lot A steel at 700°, 670°, and 640°C after 8 and 9 pct elongation. The upper limit of temperature was chosen to avoid austenite formation. The lower limit of 640°C was determined by the very long time periods that are required for recrystallization at the small deformations that were employed.

The number of recrystallized grains per unit area, n, is plotted against time in Fig. 5. In each curve the initial portion shows an exponential increase. The maximum value of n is higher when the steel is recrystallized at a higher temperature, or after greater deformation. The curves display maxima at approximately 90 pct recrystallization. At this point, new crystals are being nucleated at a rate smaller than the rate at which previously nucleated

Table I. Chemical Analysis of the Steels Investigated

Lot	C, Pct	Mn, Pct	P, Pct	S, Pct	Si, Pct
A	0.08	0.30	0.005	0.027	0.027
B	0.15	0.45	0.007	0.033	0.033



a—114 min. b—150 min. c—180 min.

d—220 min. e—360 min. f—660 min.

Fig. 3—Progress of recrystallization at 670°C in 0.08 pct C steel after 8 pct elongation. X8.

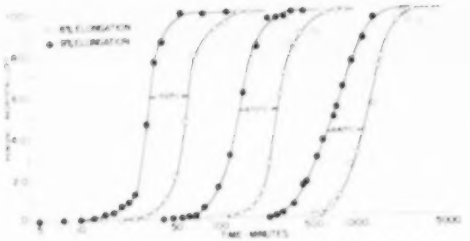


Fig. 4—Percentage recrystallized vs. time in 0.08 pct C steel.

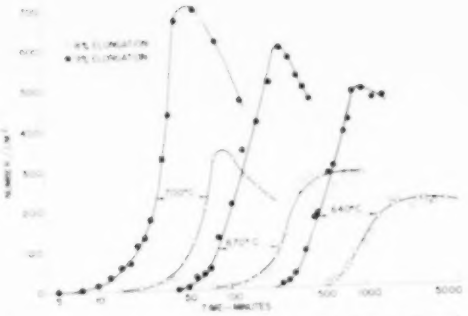


Fig. 5—Number of recrystallized grains vs. time in 0.08 pct C steel.

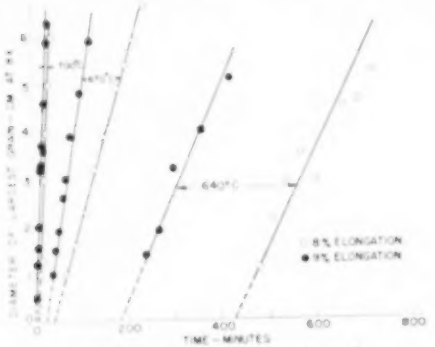


Fig. 6—Growth of the largest grain in 0.08 pct C steel.

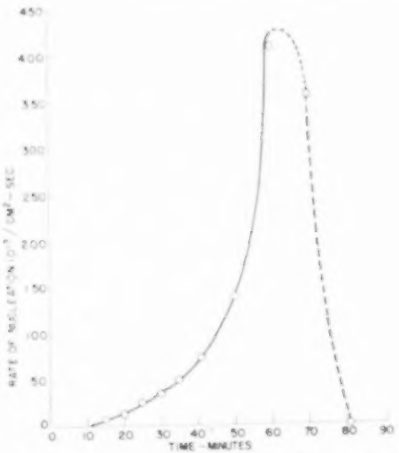


Fig. 7—Rate of nucleation vs. time in 0.08 pct C steel at 700 C after 8 pct elongation.

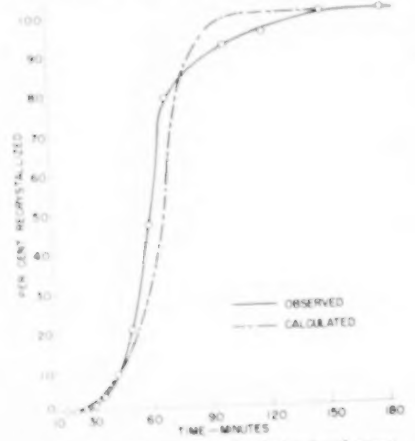
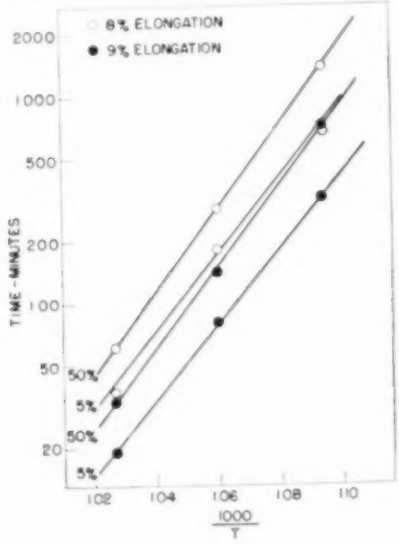


Fig. 8 above—Comparison of calculated and experimental recrystallization curves in 0.08 pct C steel at 700 C after 8 pct elongation.

Fig. 9 right—Time for 5 and 50 pct recrystallization vs. reciprocal absolute temperature in 0.08 pct C steel.



crystals are being consumed by general grain growth. Undoubtedly, grain growth, the consumption of strain-free grains by other strain-free grains, has been a competitive process during recrystallization since impingement. However, it is only toward the end of recrystallization that grain growth becomes dominant and decreases n.

In Fig. 6 the growth of the largest grain visible in each sample is shown, from whence the radial rate

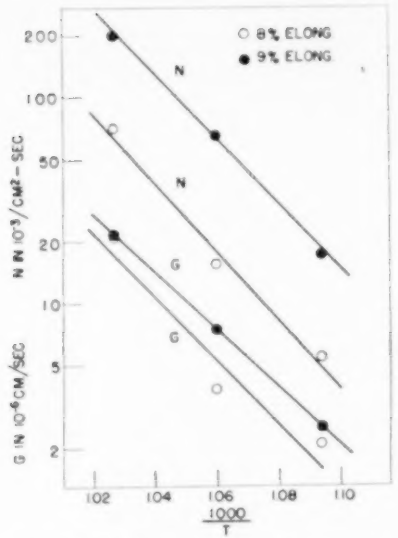


Fig. 10—N and G vs. reciprocal absolute temperature in 0.08 pct C steel.

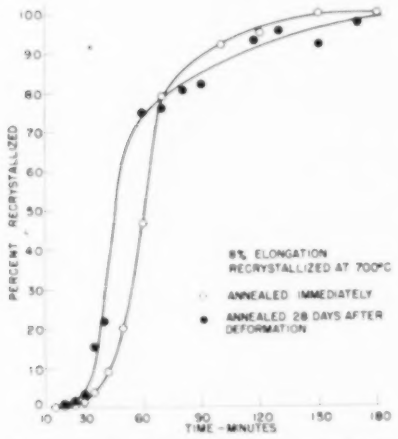


Fig. 11—Isothermal recrystallization curves showing the effect of room temperature aging in 0.08 pct C steel.

of growth, G, was determined. G decreases with decreasing recrystallization temperature and deformation. The data may be extrapolated to zero diameter to obtain incubation periods.

The slope of the n-t curve, dn/dt, was determined graphically from greatly enlarged plots similar to Fig. 5 but having a linear time scale. Dividing dn/dt by the fraction not yet recrystallized yields N, the rate of nucleation. Fig. 7 is a typical N-t plot. The increase in N during the early stages of recrystallization is described by the equation:

$$N = at^b \qquad [1]$$

where a and b are constants, and t is time. The maximum in the curve is predicted by Turnbull's[5] concept of "transient nucleation." It is brought about by the decrease in the number of available nucleation sites with the further progress of recrystallization.

There is some uncertainty in the values of N because grain growth is consuming recrystallized grains after impingement has occurred. However, during the first 30 pct recrystallization, impingement is negligible and the nucleation rate is very close to the true frequency. N-t curves were obtained for all temperatures, deformations, and compositions studied and all are similar to Fig. 7.

Theoretical Recrystallization Curve

Stanley and Mehl[1] described isothermal nucleation and growth reactions in thin sheets, where N is

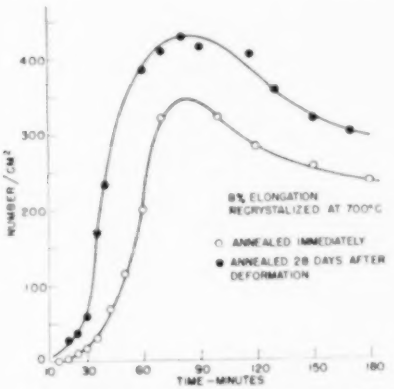


Fig. 12—Number of recrystallized grains vs. time in 0.08 pct C steel.

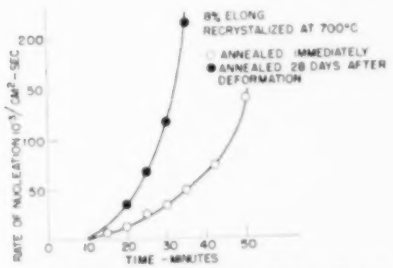


Fig. 13—Rate of nucleation vs. time in 0.08 pct C steel.

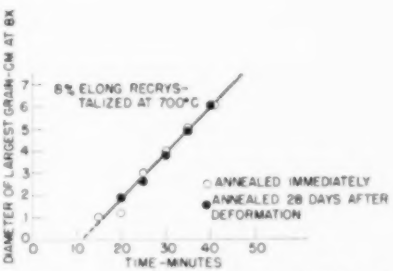

8% ELONG RECRYSTALIZED AT 700°C
○ ANNEALED IMMEDIATELY
● ANNEALED 28 DAYS AFTER DEFORMATION
DIAMETER OF LARGEST GRAIN-CM AT 8X
TIME - MINUTES

Fig. 14—Growth of the largest grain in 0.08 pct C steel.

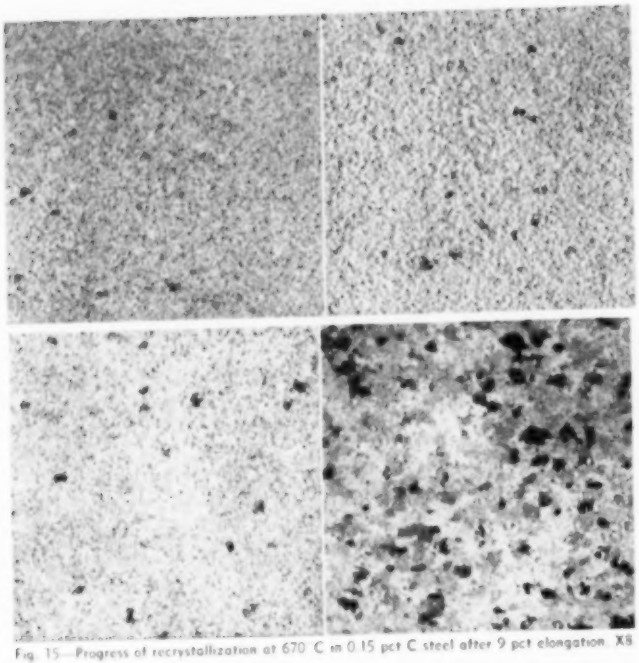


Fig. 15—Progress of recrystallization at 670 C in 0.15 pct C steel after 9 pct elongation. X8

given by eq 1 and G is constant with time, by the following equation:

$$f(t) = 1 - e^{-\frac{\pi G}{3}\left(a\frac{2b}{3}t^4 + b\frac{2b}{3}t^3 + b^2t^2\right)} \quad [2]$$

$f(t)$ is the fraction transformed; G is the growth rate; a and b are the nucleation constants, and t is the time of reaction. Since G, a, and b depend upon temperature, deformation, and composition, it is necessary to evaluate these parameters for each recrystallization experiment.

Referring to Fig. 7 it appears that eq 1 adequately describes the nucleation curve for about 55 min. Rewriting eq 1 as:

$$\ln N = \ln a + bt \quad [3]$$

and substituting values for N at 25 and 50 min, the two constants are found:

$$a = 4.98\times10^{-7} \text{ per sq cm per sec}$$
$$b = 1.11\times10^{-3} \text{ per sec}$$

Fig. 8 shows the calculated and experimentally determined recrystallization curves for one set of data. The agreement is quite good for the first 50 min or 20 pct. The data are affected by grain growth and therefore fall below the calculated curve after 85 pct recrystallization. The other calculated curves scattered a small amount to the left and right of their corresponding experimental curves but all exhibited the same effect ascribed to grain growth near the end.

Activation Energies

It is convenient to describe the rate of recrystallization in terms of the time required to reach some arbitrary percentage of the transformation. In this study a 5 pct datum point was selected as truly representative of the recrystallization process since no impingement was visible. The time required for 50 pct is included for additional comparisons. Plotting these values as determined from Fig. 4 against the reciprocal absolute temperature produced Fig. 9, which may be described by the following equations:

$$t_{5\%} = K_1 e^{Q_1/RT} \quad [4]$$

$$t_{50\%} = K_2 e^{Q_2/RT} \quad [5]$$

The time is given by t with the proper subscripts applied; K_1 and K_2 are constants; R is the gas con-

Table II. Q_1 in 0.08 Pct C Steel

Elongation, Pct	Temperature, °C	$t_{5\%}$, Min	Q_1, Cal per Mol	$t_{50\%}$, Min	Q_2, Cal per Mol
5	590	32	90,500	61	92,700
	670	130		294	
	640	690		1380	
9	590	28	93,900	53	91,900
	670	80		140	
	640	520		710	

Table III. Q_1 and Q_2 in 0.08 Pct C Steel

Elongation, Pct	Temperature, °C	N, 10^7 per Sq Cm per Sec	Q_1, Cal per Mol	G, 10^{-4} Cm per Sec	Q_2, Cal per Mol
5	590	70.2	76,100	20.8	68,100
	670	13.7		3.02	
	640	3.4		2.10	
9	590	200	72,800	21.3	63,600
	670	69.0		7.43	
	640	17.0		2.50	

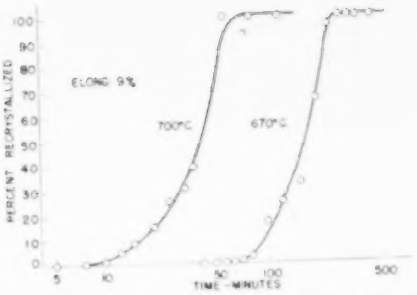


Fig. 16—Percentage recrystallized vs. time in 0.15 pct C steel.

stant; T, the absolute temperature; and Q_n, the activation energy for recrystallization. Table II presents the calculated energies. Increasing deformation causes a decrease in Q_n. Possibly Q_{recovery} is larger than Q_{recryst} because some recovery has occurred in the strained matrix during the isothermal treatment.

G and the value of N determined at 5 pct recrystallization are plotted against the reciprocal absolute temperature in Fig. 10. The points corresponding to 700° and 640°C were used to determine activation energies by means of the following expressions:

$$N = K_1 e^{-Q_N/RT} \quad [6]$$

$$G = G_1 e^{-Q_G/RT} \quad [7]$$

N and G are the rates of nucleation and growth, respectively; K_1 and G_1 are constants; and Q_N and Q_G are the activation energies for nucleation and growth, respectively. Table III contains the plotted data and the calculated activation energies.

Strain Aging

Samples of lot A steel were held at room temperature 28 days after deformation before they were recrystallized. Figs. 11 to 14 compare the recrystallization behavior of the aged samples with material recrystallized directly after deformation. Aging increased N and caused essentially no change in G. Hence, the greater part of recrystallization occurred in a shorter time in the aged steel. These effects are similar in kind to those produced by increasing the deformation from 8 to 9 pct and recrystallizing at 700°C.

Recrystallization of 0.15 Pct C Steel

To determine the effect of increased pearlite volume on recrystallization, lot B strips were elongated 9 pct and recrystallized at 670° and 700°C. Fig. 15 shows the course of recrystallization at 670°C. The two isothermal curves presented in Fig. 16 illustrate the sigmasoidal shape shown earlier in Fig. 4 which is characteristic of isothermal reaction curves for general nucleation. Fig. 17 shows crystal growth.

The large number of crystals which formed during recrystallization were counted and their number, n, plotted against time in Fig. 18. Well-defined maxima are observed at 700° and 670°C. It may be restated here that each point is the average value obtained from six samples, each of which was cut from a different elongated strip.

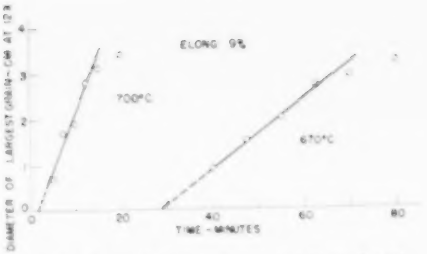


Fig. 17—Growth of the largest grain in 0.15 pct C steel.

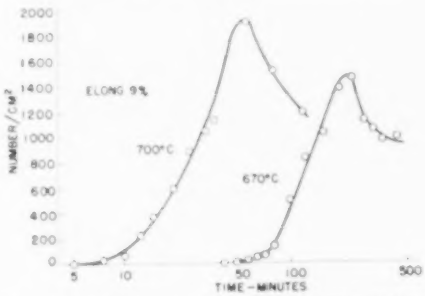


Fig. 18—Number of recrystallized grains vs. time in 0.15 pct C steel.

The times required for 5 and 50 pct recrystallization were determined from Fig. 16. Using eqs 4 and 5 activation energies were calculated and listed in Table IV.

Values of N determined at 5 pct recrystallization and of G were substituted in eqs 6 and 7 to obtain activation energies for nucleation, Q_N, and for growth, Q_G. These are listed in Table V.

Discussion

Clarebrough[7] investigated the deformation and recrystallization characteristics of two phase alloys in which the second or β phase was much harder than the matrix. He found that the β disrupted the strain pattern within the matrix, causing stress concentrations near the β particles. For a given external deformation, the average stress level in the matrix was markedly raised when the volume of β increased between 0 and 20 pct. In the present case, pearlite may be likened to a hard, β phase. Increasing the pearlite volume from 10 to 19 pct (from lot A to lot B steel) served to increase the average stress level of the ferrite matrix for the external strain of 9 pct. Since nucleation rates were demonstrated in Table III to increase greatly with deformation, increasing

Table IV. Q_n in 0.15 Pct C Steel, Elongated 9 Pct

Temperature, °C	$t_{5\%}$, Min	$Q_{5\%}$, Cal per Mol	$t_{50\%}$, Min	$Q_{50\%}$, Cal per Mol
700	15	98,000	45	100,000
670	80		190	

Table V. Q_N and Q_G in 0.15 Pct C Steel, Elongated 9 Pct

Temperature, °C	N, 10^6 per Cm Sec	Q_N, Cal per Mol	G, 10^{-4} Cm per Sec	Q_G, Cal per Mol
700	750	90,200	16.2	76,400
670	164		4.5	

Fig. 19—0.08 pct C steel elongated 8 pct and held at 670 C for 220 min. X500

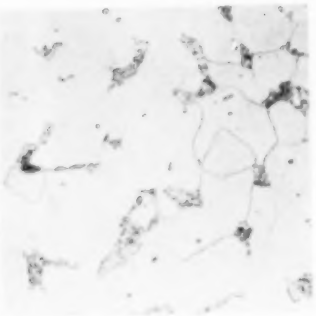


Fig. 20—0.15 pct C steel elongated 9 pct and held at 670 C for 125 min. X500

the stress level of ferrite may account for the great increase in N observed in lot B steel.

Fig. 19 shows a large recrystallized ferrite grain growing into the deformed, starting material of lot A steel. The carbides of the former pearlite nodules have been spheroidized in the fine grained matrix. Spheroidization apparently occurred in the matrix material under the conditions of deformation, temperature, and time studied. The spheroidite areas are skirted by the advancing ferrite boundary. After the carbides have been surrounded and the boundary rejoins itself, further growth continues. Several small ferrite grains of the original structure remain in the large crystal. These included grains give rise to the spotted appearance of the large crystals in Figs. 3d and e. The number of included grains diminishes after prolonged heating, Fig. 3f.

Fig. 20 shows the interference of carbides on the growth of the ferrite boundary in lot B steel. All the spheroidite areas are undercut and transferred to the large crystal after complete encirclement.

Increased deformation causes a greater increase in nucleation rate than in growth rate as demonstrated in Fig. 10. Thus, the maximum number of recrystallized grains produced after 9 pct extension is greater than that produced after 8 pct, see Fig. 5. These facts are consistent with the concept that recrystallization nuclei form in the most highly stressed points in the cold worked matrix. The decrease in activation energies for recrystallization, nucleation, and growth with increased deformation similarly support this concept.

Turnbull[7] recently derived the following expression relating G_o, the constant in eq 7, with the jump distance of atoms in diffusion, a, the energy stored in the lattice by cold working, ΔF, and the entropy of activation for grain boundary migration, $(\Delta S_i)_o$:

$$G_o = a \times \left(\frac{kT}{h}\right)\left(\frac{\Delta F}{RT}\right) e^{-(\Delta S_i)_o/R} \qquad [8]$$

where k and h are the Boltzmann and Planck constants, respectively. Assuming a to be 2.5×10^{-8} cm for iron atoms, and ΔF to be 8 and 9 cal per mol for 8 and 9 pct elongation, respectively, $(\Delta S_i)_o$ may be calculated for lots A and B steels.

The free energy of activation for grain boundary migration, $(\Delta F_i)_o$, may then be found, using the equation:

$$(\Delta F_i)_o = Q_o - T(\Delta S_i)_o - RT \qquad [9]$$

Table VI lists the calculated values of G_o, Q_o, $(\Delta S_i)_o$, and $(\Delta F_i)_o$ for steel and silicon iron, as well as the energy, entropy, and free energy of activation for lattice self-diffusion of pure iron.

It is interesting to note that the values of $(\Delta F_i)_o$ for silicon iron and for steel are the same within the experimental error for all the compositions and strains investigated. $(\Delta F_i)_o$ is approximately equal to three-fourths of the free energy of activation for lattice self-diffusion in iron. The difference between the two free energies is smaller for steel than for silver, where Turnbull[7] reported the ratio to be about one-half.

Summary

1—Isothermal recrystallization curves for 0.08 pct C steel at 700°, 670°, and 640°C after 8 and 9 pct elongation are presented. Similar curves are given for 0.15 pct C steel recrystallized at 700° and 670°C after 9 pct elongation. Both increased temperature and deformation increase N and G and thereby increase the rate of recrystallization. Activation energies for nucleation, growth, and recrystallization are calculated.

2—Strain aging in 0.08 pct C steel increases N and leaves G unchanged.

3—Increased pearlite volume increases N and decreases G.

4—Good agreement with the theoretical recrystallization rate equation derived for the two-dimensional case by Stanley and Mehl[1] is reached in the present data.

5—Evidence of the overlapping of recrystallization and general grain growth is presented. Grain growth apparently decreases the number of grains after approximately 90 pct recrystallization has occurred.

6—All values of G remain constant with time

Table VI. Comparison of Energy, Entropy, and Free Energy of Activation in Self-Diffusion and Boundary Migration

Material	Elongation Pct	Temperature, °C	G_o, cm per Sec	$(\Delta S_i)_o$, Cal per Mol. Deg	$(\Delta S_{sd})_o$, Cal per Mol. Deg	Q_o, Kcal per Mol	Q_{sd}, Kcal per Mol	$(\Delta F_i)_o$, Kcal per Mol	$(\Delta F_{sd})_o$, Kcal per Mol
Silicon iron[6]	7	700	1.7×10^{-7}	13	34.7	59.7	73.0	45.1	37.3
Iron[6]		700					68.1		36.0
0.08 pct C steel	8	700	3.0×10^{-7}		31.0		63.6		35.7
0.08 pct C steel	9	700	4.1×10^{-7}		29.7		76.4		36.3
0.15 pct C steel	9	700	2.2×10^{-7}		39.2				

until grain impingement occurs. Nucleation rate vs. time plots increase exponentially at first, pass through a maximum, and decrease to zero.

7—The data of this investigation are consistent with the concept that high stress points in the deformed structure serve as loci for nucleus formation in recrystallization.

8—In grain boundary migration in steel, the free energy of activation is significantly smaller than in lattice self-diffusion in iron.

Acknowledgments

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Technical Note

Do Metals Recrystallize?

by Paul A. Beck

ACCORDING to the traditional definition,[1] recrystallization is a process taking place upon annealing of cold worked metals, characterized by the appearance of new strain-free grains, growing at the expense of the cold worked grains until ultimately the new crystals completely replace the cold worked structure. In metals like brass this process was observed long ago to take place simultaneously with the return of the mechanical properties to those characteristic of well annealed material. The above definition implicitly assumes that the matrix in which the new grains are growing is essentially still in the cold worked condition at the time it is absorbed by the new grains, i.e., that the energy stored in the metal during cold working is not greatly decreased by recovery, prior to recrystallization. Accordingly, the bulk of this energy is assumed to serve as the driving force for the process of recrystallization.

Recently, a great deal of evidence accumulated, indicating that the traditional concept may be considerably in error. Suzuki[2] found that by far the largest portion of the stored energy of cold work in compressed polycrystalline copper is released in the early stages of annealing, well in advance of recrystallization. Thus, the new recrystallized grains are undoubtedly growing in a matrix which is, at least energetically, no longer in the cold worked condition, but has nearly returned to the annealed state. It is true that in Suzuki's experiments the major hardness changes due to annealing were observed to take place concurrently with the formation and growth of the new grains, but this process apparently involved the release of only a minor residual fraction of the stored energy of cold work.

Confirming in this respect the views of Wood,[3] several recent investigations by various techniques lead to the conclusion that the grains of many, if not all, metals in the cold worked condition consist of small, slightly disoriented "crystallites" or "subgrains".* (After appreciable deformation at room temperature, the subgrain size in copper appears to be about 7.10^{-5} cm and in high purity aluminum about 2.10^{-4} cm.) Recent investigations which demonstrated this phenomenon most convincingly are those of Heidenreich[4] with hammered high purity aluminum, of P. B. Hirsch and collaborators[5] with cold worked polycrystalline aluminum, copper, nickel, iron, gold, etc., and of Warren and Averbach[6] with a rolled copper plus 2 pct Si single crystal. In addition to the existence of slightly disoriented subgrains, the cumulative evidence from these investigations also shows that in the cold worked condition the subgrains themselves are severely strained. With regard to the early stages of annealing, Heidenreich's results indicate that within the subgrains of hammered high purity aluminum the strain gradually disappears, without discernible migration of the subboundaries. This recovery process presumably accounts for the major portion of the energy release

* Whether the subgrains form as a direct result of deformation, according to the views of Wood and his collaborators,[3] or practically simultaneously, but in effect after plastic deformation, by means of an annealing process, namely polygonization, as described by Cahn,[7] is not important for the purposes of the present discussion.

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measured by Suzuki. Another process, which sometimes takes place prior to recrystallization is subgrain growth. This was observed, for instance, in bent aluminum crystals by Guinier and Tennevin,[7] in bent silicon-iron crystals by Dunn and Daniels,[8] and in severely rolled polycrystalline aluminum by Beck and Hu.[9] Subgrain growth apparently requires higher annealing temperature (or much longer time) than the recovery process mentioned, and in some cases, as in Heidenreich's experiments, it may be largely forestalled by recrystallization, if the latter sets in relatively early. What part of the energy release on annealing is contributed by subgrain growth is at present not clear.

Although in cold worked copper extensive recovery precedes recrystallization, the major mechanical property changes resulting from annealing take place concurrently with recrystallization. It appears, however, from recent research that in many cases even these mechanical property changes take place prior to recrystallization. It was found by means of a combination of texture determination and of microscopic technique[10] that after annealing which suffices to restore the soft annealed mechanical properties in severely rolled aluminum, there is only partial recrystallization. In many local areas the annealing process takes place by the alternative mechanism, which has been designated by Crussard as "recrystallization in situ;"[11] recovery of the subgrains is here followed by subgrain growth instead of by recrystallization involving the growth of new grains of a different orientation. The volume fraction of recrystallized material increases gradually with the annealing temperature in a temperature range far exceeding that necessary for complete softening. For rolled beryllium,[12] cross rolled molybdenum,[13] and for silicon-iron crystals of certain orientations,[14] the textures in the completely annealed condition are reported to be essentially the same as those in the cold rolled condition. By analogy with the findings for aluminum,[10] it may be concluded from the retainment on annealing of these essentially single orientation textures that softening here is achieved by recovery and subgrain growth, which does not involve reorientation. In many cases recrystallization involving reorientation is observed to take place at a higher annealing temperature than that necessary for softening. Where softening occurs by recrystallization, as in copper and brass, the mechanical strength retained in spite of essentially complete recovery should be presumably attributed to the small size of the subgrains, i.e., to the lack of appreciable subgrain growth prior to recrystallization. On the other hand, in the case of rolled molybdenum and silicon-iron crystals of certain orientations apparently considerable subgrain growth (and complete softening) occurs before "recrystallization."

A conclusion that may be drawn from these investigations is that in many cases (and probably always) the new grains formed on annealing in deformed metals do not grow at the expense of "deformed material," as was supposed in the traditional picture of recrystallization. Not only is most of the stored energy of cold work released prior to "recrystallization," but in many cases softening also takes place in this early stage of the annealing process. Insofar as the available data permit generalization, it appears that metals do not recrystallize in the traditional sense. The microscopically observed "recrystallization" now appears to be a process fundamentally akin to a type of grain growth ("coarsening," "discontinuous" grain growth," or "secondary recrystallization") which occurs in substantially strain-free matrix with strong single orientation texture,[15] grains with an orientation strongly deviating from that of the matrix grow much larger than the matrix grains. The alternative mechanism for complete softening, namely subgrain growth, resembles continuous or gradual grain growth, where the type of grain size distribution and the preferred orientation do not change appreciably. In both processes the total interface area and also the interface energy per unit volume decrease. Thus, recent evidence tends to support Smith's suggestion[16] that the driving energy of "recrystallization" is interface energy associated with the subboundaries.

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Observations on the Lattice Parameters of the Alpha And TiO Phases in the Titanium-Oxygen System

by W. Rostoker

A STUDY of the titanium-oxygen system[1] involved an associated series of measurements of the lattice parameters of the α and TiO phases. The results permit some interesting deductions which are herein reported. A comprehensive survey of the physical properties of the phases in this alloy system has been made by Ehrlich.[1] However, only impure titanium was available at that time, so that some revision of his measurements is to be expected.

The lattice parameters were calculated from the high angle lines of Debye-Scherrer patterns taken in a 14 cm camera and using filtered CuKα radiation. The specimens were prepared largely by crushing and screening of lump samples which had been quenched from elevated temperatures. Only in the case of low oxygen contents was it necessary to resort to filing and annealing.

The results of the lattice parameter studies are graphically presented in Figs. 1 and 2. It will be seen that oxygen produces a pronounced distortion of the c parameter of the α phase (hexagonal close-packed). The trend is in general agreement with Ehrlich's work, although the divergence of actual parameter values strongly suggests that his titanium was very impure. It will be noted that the α phase of titanium can tolerate the unusually high saturation solubility of about 34 atomic pct O. By virtue of this unique effect, it is possible to make a calculation of the effective atomic diameter of oxygen when dissolved in a lattice with metallic bonding. This has not been possible before.

Ehrlich's[2] density measurements demonstrated that oxygen occupies interstitial positions in the α lattice and the trend of the lattice parameters would certainly support this. In a hexagonal close-packed unit cell the largest interstitial positions lie at (2/3, 1/3, 1/4) and (2/3, 1/3, 3/4). Accordingly, if both of these positions were occupied, the ratio of titanium to oxygen would be 1:1. The extrapolated c parameter may be taken as between 4.93 and 4.99A. The a parameter appears to reach a constant value of 2.955A at low oxygen contents. The distance of the center of a titanium atom site from the center of an interstitial atom site is $\sqrt{\frac{c^2}{16} + \frac{a^2}{3}}$. Then the atomic diameter of the oxygen atom is represented by the function:

$$2\left[\sqrt{\frac{c^2}{16} + \frac{a^2}{3}} - 1.448\right]$$

where the radius of the titanium atom is 1.448A.

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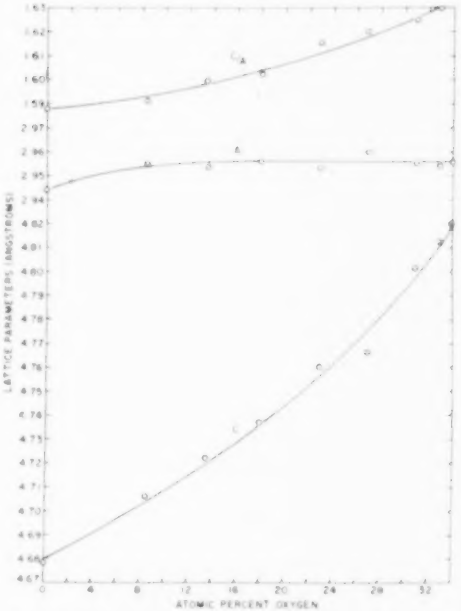

Fig. 1—Lattice parameters of the α solid solution in the Ti-O system.

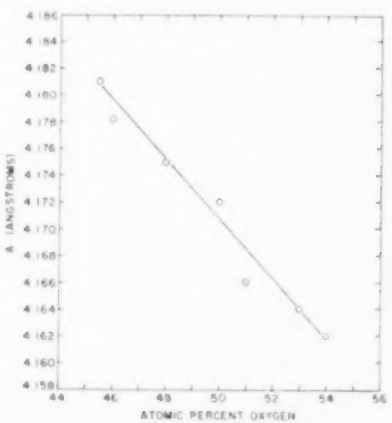

Fig. 2—Lattice parameters of the TiO phase in the Ti-O system.

and c and a are the estimated values of the lattice parameters at the 50-50 atomic proportion. The calculated diameter of the oxygen atom so obtained is between 1.31 and 1.33A. This value is surprisingly close to the single bond diameter of 1.32A reported by Pauling[3] as obtained in structures of the covalent type.

The TiO phase, in confirmation of Ehrlich's work, has a cubic structure of the NaCl type. From density measurements Ehrlich has shown that the large range of miscibility may be interpreted in terms of extra titanium and oxygen vacant sites, respectively, on the high and low oxygen sides of the TiO composition. However, Ehrlich considered this phase to possess an ionic type of bonding and the vacant site phenomenon required the postulate of mixtures of monovalent and divalent and of divalent and trivalent titanium. Consideration of certain factors seems to indicate that the NaCl structure exhibited derives from factors other than ionic bonding.

From Pauling's data[3] the diameter of the O^{--} ion is 2.80A. The diameter of the divalent titanium atom may be calculated from an expression used by Pauling:[3]

$$R = \left(\frac{nB}{AZ}\right)^{n}$$

where R is the ionic radius; Z, the ionic charge number; and n, B, and A are constants ($n = 9$). Whence:

$$D_{Ti^{++}} = D_{O^{--}}\left(\frac{Z_{O^{--}}}{Z_{Ti^{++}}}\right)^{\frac{n-1}{n}} = 3.45\text{A}$$

The assumption has been made here that titanium in the pure state or in primary solid solutions is a tetravalent metal. Support has been found for this[4] from a consideration of the Brillouin zone and lattice parameters of the α primary solid solution in the Ti-Al system. A calculation of the lattice parameter of the TiO phase, assuming ionic bonding, yields the value 6.25A, which is considerably in excess of that observed. On the other hand, using the diameter of tetravalent titanium and of the oxygen atom derived from the α phase lattice parameters gives a value of 4.22A, which is very close to that observed.

As a further check on the hypothesis that the TiO phase has metallic bonding, a measurement was made of electrical resistivity. This measurement was made on a cast button of variable dimensions so that the results are likely to be in error on the high side by a factor of as much as two. The resistivity obtained was in the order of 300 microhm-cm, which definitely excludes the possibility of either covalent or ionic bonding.

The magnitude of resistivity suggests a full Brillouin zone condition. Because of the low scattering power of oxygen, the TiO structure may be considered as a face-centered cubic lattice of titanium atoms. According to Raynor et al.,[5] the second Brillouin zone for a face-centered cubic structure can contain 4 electrons per atom when geometrically full. An inscribed sphere corresponds to 2.49 electrons per atom but, as Raynor points out, the Fermi distribution within the second zone would be expected to be far from spherical. Accordingly, the full (in the sense of just prior to an overlap) second zone may be expected to contain between 2.49 and 4 electrons per atom. From the deduction that the TiO structure is not ionic, it must be concluded that oxygen is a donor, rather than an acceptor, of electrons. Under the circumstances, the electron to atom ratio must reasonably lie between 2.5 and 4 if the oxygen atom gives 1 to 4 electrons, respectively, as free electrons to the lattice.

Table I. Calculation of Electronic Concentrations per Unit Cell

Atomic Pct Oxygen	Ehrlich's Estimates of Sites Occupied: Pct Ti	Pct O	Electrons per Unit Cell
47	74	99 (100)	23.66 (23.84)
50	77	99	23.84
52.6	81	91	23.66
54	85	85	23.80
56	90 (100)	80	23.28 (23.90)

Thus far, conclusions have been based on rather simple deductions. It might be profitable, though controversial, to extend the discussion of the positive oxygen ion beyond the bounds strictly warranted by the existing data. If oxygen were present as an O^{--} ion in the TiO structure, then the electronic concentration per atom would be 3. Aluminum is another case of a trivalent metal[6] with a face-centered cubic structure. It is difficult to conceive under such circumstances how TiO and aluminum should have such widely different resistivities. The author would choose to exclude the possibility of O^{--} on these grounds.

The vacancies of oxygen sites and titanium sites, respectively, on either side of the TiO composition has an analogy in the occurrence of vacant nickel sites in the NiAl phase.[7] In the latter case, a satisfactory explanation has been found based on the preservation of a critical electronic concentration per unit cell. The same condition may be shown to apply to the miscibility range of the TiO phase. Using Ehrlich's[2] estimates of the percentages of titanium and oxygen sites occupied at various compositions and quite arbitrarily choosing the oxygen ion to be O^{--}, the electronic concentrations per unit cell have been calculated. It will be recognized that using an O^{-} ion would yield the same trend. The results of these calculations, shown in Table I, show the electronic concentrations are almost constant, especially (as shown in brackets) if it is assumed that Ehrlich's estimates are slightly in error in two cases. This would seem to strengthen the analogy with the NiAl phase and thereby render its explanation applicable to the case of TiO. Also, the possibility of O^{-} ions is obviated, because vacancy of sites would not be necessary to preserve a constant electronic concentration.

Two alternatives remain, namely, O^{-} or O^{--} ions. Without further information on the densities of states at electronic concentrations of 2.5 and 3.5 e/a, no further speculation is warranted.

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System Molybdenum-Boron and Some Properties of The Molybdenum-Borides

by Robert Steinitz, Ira Binder, and David Moskowitz

THE hard refractory borides of the transition elements of the 4th, 5th, and 6th groups of the Periodic System have been the subject of a number of recent investigations.[1-5] It is well known now that most of these elements form several different borides, and Kiessling[1] has summarized the rules which govern to some extent the arrangements of the boron atoms in the various structures. Melting points of a few borides have been published.[6] The systems Fe-B, Ni-B, and Co-B have been reported,[7] but, as these borides are rather low melting, they are outside of the groups of boron compounds considered here. Brewer[8] has tested the stability of various borides and estimated a number of eutectic temperatures between different borides, but in no case was the complete system of a transition metal and boron investigated. The phase diagram becomes of special importance if the preparation of the borides from the elements in powdered form is considered; the lowest eutectic temperature will determine the first appearance of a liquid phase. Also, the knowledge of high temperature phases, if they exist, is important for the preparation of bodies from these borides by hot pressing or sintering.

During the investigation of various metal borides,[5] it was found that there were more boride phases existing in the Mo-B system than reported by Kiessling.[1] They occur, however, only at temperatures above 1500° C and were, therefore, not found by him. This led to a study of the equilibrium diagram of the Mo-B system, ranging from 0 to 25 pct B and from room temperature to the liquidus. Part of this investigation was reported during the "Research in Progress" session at the 1952 Annual Meeting of the AIME.[9]

Raw Materials and Preparation of the Borides

The raw materials used were commercial molybdenum and boron powder, both supplied by the Molybdenum Corp. of America. The molybdenum powder was 99+ pct pure, while the boron powder contained about 83 to 85 pct B. A large percentage of the impurities in this powder was oxygen, with the rest formed by iron, calcium, and unknown substances. The low purity of the boron used was, however, not considered detrimental to the final product, as most of the impurities evaporated at the high temperatures at which the borides were formed. The final product always had a minimum purity of 96 to 98 pct (figured as molybdenum and boron), with carbon, iron, and probably oxygen being the remaining products. Carbon is usually present as graphite. The chemical analyses always confirmed the compositions which corresponded to the crystallographic structures as determined by X-ray diffraction, and the boron content of the finished product agreed closely with that of the starting mixture; no boron was lost during the boride preparation. The chemical analysis methods employed for molybdenum and boron were previously described by Blumenthal.[10,11]

The powders were mixed by hand in the desired proportions, compressed at room temperature under low pressure, and then heated under hydrogen to about 1500° to 1700° C in a graphite crucible to form the borides. Usually, the three well-known borides Mo_2B, MoB, and MoB_2, which are stable at room temperatures, were prepared in this way, and all other compositions were made by mixing these borides in various ratios or by the addition of molybdenum or boron powders for the very low or very high boron contents. Preparation of two-phase compositions directly from the elemental powders was tried only occasionally to check whether equilibrium could be reached in this way.

Experimental Procedures

The stable borides were mixed in the desired ratios and heated under hydrogen in graphite crucibles to various temperatures. The well insulated crucibles were heated in a high frequency induction furnace. Special care was taken to obtain exact temperature measurement, which proved much more difficult than originally anticipated. It is believed that individual temperature measurements have an error of less than ±25° C, while melting or transformation temperatures are accurate within ±50° C. The temperatures were measured with an optical pyrometer which was aimed at the closed end of a graphite tube extending down into the crucible, close to the samples. Attempts to measure directly through the hydrogen exit stack failed. The crucible arrangement is shown in Fig. 1. Heating was done at a slow rate to be sure that the temperature inside the crucible was uniform. The specimens were kept at the final temperature for about 30 min.

For the investigation of high temperature phases, some samples were quenched. They were heated, without atmosphere protection, in a very small graphite crucible which could be rapidly removed from the high frequency coil, and dropped into water. These quenched samples were afterwards annealed to establish the equilibrium at lower temperatures.

The melting points or the positions of the solidus and liquidus lines were determined by heating the specimens to various temperatures and examining them at room temperature for evidence of a liquid phase. These results were checked later on by thermal arrest curves, especially to determine the exact position of the eutectic temperature line. For this purpose about 200 g of the boride were melted in a graphite crucible, in an arrangement similar to Fig. 1. Slow cooling was assured by very good

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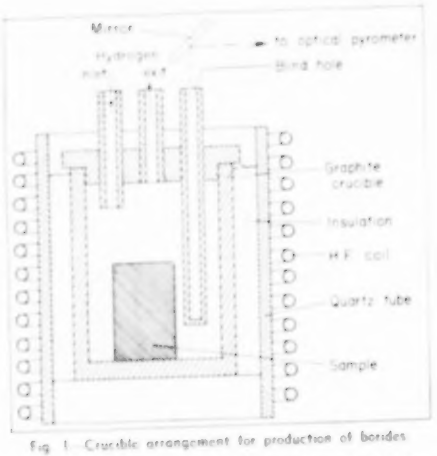

Fig. 1—Crucible arrangement for production of borides

insulation of the crucible. A Leeds and Northrup Rayotube measured the temperature and recorded it on a Leeds and Northrup Speedomax instrument. A thermal arrest curve for the cooling of MoB is shown in Fig. 2, giving a melting point of 2180°C for this boride. The Rayotube was calibrated against the optical pyrometers used for other experiments of this investigation.

All samples were checked for the phases present by X-ray diffraction. The patterns observed were compared with those published by Kiessling[1] for the three room temperature molybdenum-boride phases or with other known boride structures, such as CrB or ThB. By such a comparison, all structures could be identified and the parameters determined.

The preparation of metallographic specimens proved to be extremely difficult due to the high hardness and brittleness of the samples. No clear picture of the structure could be obtained under the microscope. This method of investigation was, therefore, excluded as unreliable. Occasional checks of the electrical resistivity served to support the findings about the existence of a high temperature phase in some samples.

Room Temperature Phases

All phases described by Kiessling could be reproduced without difficulties. The X-ray patterns were calculated from his data and found to be in excellent agreement with those obtained from borides prepared for this investigation. These borides are Mo_2B, MoB, and MoB_2. For the ranges of homogeneity of these borides, Kiessling's values were accepted. The rather large range of MoB seems to be assured, though no exact determination of it was tried here. All room temperature phases are stable up to at least 1600°C when the first transformation occurs in Mo_2B. No phase with a boron content higher than MoB_2 could be found, despite several attempts to produce MoB_3 or MoB_4 structures which might have been expected.[1]

Mo_2B exists in the stoichiometric composition of 5.3 pct B. It does not undergo any change up to 2000°C, when it starts melting in a peritectic reaction forming liquid and a new compound Mo_2B_3 which will be discussed later. A material of this composition is completely liquid at 2060°C.

MoB has an extended homogeneity range including the composition of 10.1 pct B which corresponds to this formula. The investigation of samples which were either molten or heated above 2000°C revealed the existence of a new modification of this compound. This so-called β-MoB is isomorphous with CrB, while the room temperature modification has its own characteristic structure. The high temperature form could be retained by quenching and changed back to the stable structure by long time annealing at temperatures as low as 1100°C. The β modification seems to exist, however, only for compositions with the stoichiometric amount of boron or with an excess of it. It was never found in samples deficient in boron. This might be of theoretical importance though no explanation can be offered. The melting point of MoB is 2180°C.

Mo_2B_3 exists only with a deficiency of boron. Its range covers compositions from about 19.5 to 20.8 pct B, while its formula would require 22 pct. It undergoes a transformation at 1600°C, where the structure becomes isomorphous with the well-known diboride structure. This modification, which has been described,[1] is therefore called MoB_2. This formula is meant to designate only the structure, not the exact chemical composition. The range for MoB_2 is similar to that of Mo_2B_3, while a composition with 18.4 pct B (corresponding to MoB$_2$) is definitely located in the two-phase field at all temperatures.

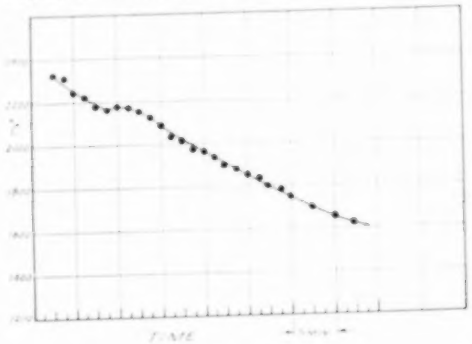

Fig. 2—Thermal arrest curve for MoB

MoB could also be retained at room temperature by quenching, or relatively fast cooling. It is easier to obtain than the higher forming high temperature modification of MoB. The melting point of MoB is 2100°C.

System Molybdenum-Boron

A tentative diagram of the Mo-B system is shown in Fig. 3. Although many of the finer details have not been studied, the diagram is drawn to be consistent with the experimentally observed data and to show the correct relative positions of the several single-phase fields. The temperatures shown are those actually measured.

Samples with as little as 1 pct B showed clearly the presence of Mo_2B, so that no lower boride seems to exist. The two-phase field extends from very small amounts of boron to Mo_2B. The solubility of boron in molybdenum metal was not determined. In these two-phase samples, some or all of the molybdenum metal was changed to the carbide Mo$_2$C during heat treatment. This could not be prevented, but it is significant that carbon only showed an influence where either free metal or free boron was present. No carbide was found to coexist with MoB or the

two-phase structures containing MoB. This stability of the molybdenum-borides against carbon seems to be characteristic for the borides of the metals of the 6th group.[7] The peritectic temperature for Mo_2B is 2000°C. The eutectic composition, determined by extrapolation, contains about 1 pct B.

At lower temperatures, compositions containing 5.3 to 9.7 pct B consist of the two phases: Mo_2B and MoB. There exists, however, another boride structure, Mo_2B_5, at temperatures above 1850°C. This boride is formed by the peritectic decomposition of Mo_2B. It could not be obtained in the pure form at room temperature. It melts at 2070°C and is stable only down to 1850°C. The exact range for this boride, which has not been reported previously, is not known. Its structure is, however, isomorphous with Cr_2B_5,[8] and its position between Mo_2B and MoB makes it probable that the composition corresponds to Mo_2B_5.

The partial system Mo-MoB is shown in Fig. 4 which indicates the experimental results on which the explanation of the system was based. Different structures present and conditions of melting are indicated. As mentioned before, no change to β-MoB could be found for compositions containing less than 10 pct B.

Compositions between 10.7 and 19.5 pct B show two phases; they consist of MoB and Mo_2B_5, or their high temperature modifications, depending on the temperature. A eutectic exists at about 14 pct B and 2060°C, at a temperature slightly below the melting point of Mo_2B_5.

If more boron than about 21 pct was added, B_4C, but no higher molybdenum-boride was formed. Glaser[9] pointed out that some borides cannot be formed in the presence of carbon. Though all molybdenum-borides described so far were stable in contact with graphite, special attempts were made to produce higher molybdenum-borides without the use of graphite material. However, no higher borides than Mo_2B_5 were formed even under these conditions. The two-phase region between Mo_2B_5 and boron was not investigated for the position of the eutectic.

Structures of Molybdenum-Borides

Four molybdenum-borides exist in the Mo-B system, of which two show phase transformations. These six different structures are given in Table I together with type and lattice parameters of the crystal structure and the composition and temperature range in which they exist. Kiessling's data[1] are incorporated in this table.

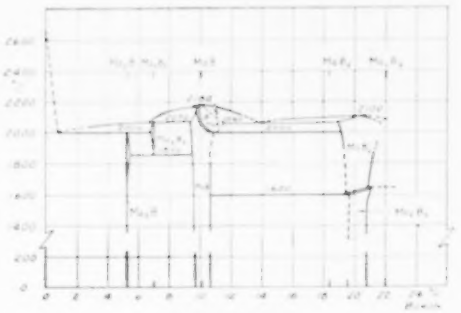

Fig. 3—Mo-B system.

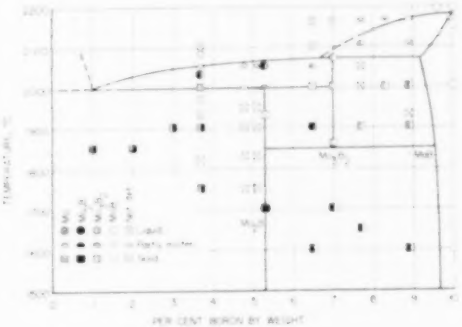

Fig. 4—Mo-MoB partial system.

The similarity of the high temperature structures of the molybdenum-borides with the room temperature structures of the chromium-borides is great. However, a boride corresponding to Cr_3B_2 could not be found.[10] Recently a wolfram-boride modification isomorphous with CrB was also detected.[11] The transition metals of the 6th group of the Periodic System obviously show close relationships in the structure of their borides.

The high temperature forms, β-MoB and MoB, can be stabilized down to room temperature by the addition of other metal borides. CrB and CrB_2, for

Table I. Crystal Structures and Stability Ranges of the Molybdenum-Borides

Nominal Compound	Stoichiometric Composition, Pct B	Crystal Structure		Stability Range	
		Type	Lattice	Composition, Pct B	Temperature, °C
Mo_2B	5.3	Fe_2B	Tetragonal a_0=5.54Å c_0=4.74Å	5.3	Room—2000
Mo_2B_5	7.0	Cr_2B_5	Not determined	7.0	1850-2070
MoB	10.1	MoB	Tetragonal a_0=3.11Å c_0=16.97Å	9.7-10.7 9.7—approx. 10.0	Room—2000 Room—2180
β-MoB	10.1	CrB	Orthorhombic a_0=3.16Å b_0=8.61Å c_0=3.08Å	Approx. 10.0-10.7	2000-2180
MoB_2	18.4	Diboride	Hexagonal a_0=3.06Å c_0=3.10Å	Approx. 19.5-20.8	1800-2100
Mo_2B_5	22.0	Mo_2B_5	Rhombohedral Hexagonal axes: a_0=3.01Å c_0=20.93Å	Approx. 19.5-20.8	Room—1600

Note: MoB includes stoichiometric composition. Neither Mo_2B_5 nor MoB exist in the stoichiometric composition.

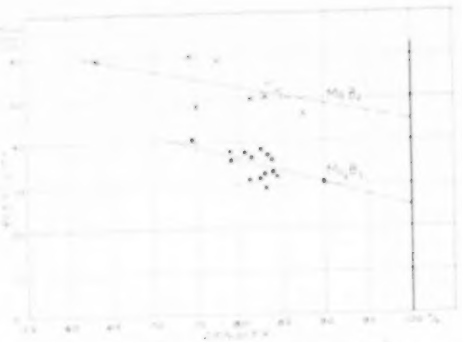

Fig. 5—Resistivity vs. density for Mo_2B and MoB.

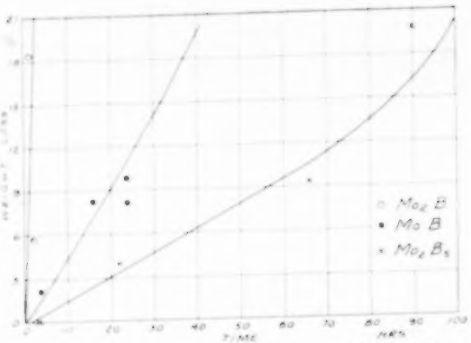

Fig. 6—Weight loss by oxidation at 1000°C in air for molybdenum borides.

example, form solid solutions with the corresponding molybdenum-borides, resulting in crystal structures at room temperature which would correspond to the high temperature modifications.

Discussion

The investigation of the molybdenum-borides up to their melting points and of the two-phase regions between them has revealed the existence of three more structures than reported in the most detailed previous publication.[1] This made it clear that a complete picture of all the borides of a metal can only be obtained by using much higher temperatures than generally are employed. Even 1200°C is a low temperature for these very high melting substances. Furthermore, the influence of heating conditions such as atmosphere or crucible materials has to be considered. It was found here that graphite does not interfere with the formation of the molybdenum-borides, but this is undoubtedly different for borides of metals of the 4th and 5th groups.[2] It is difficult, however, to reach such high temperatures without the use of graphite crucibles or heating tubes.

Brewer[3] had found that W$_2$B would decompose in the presence of carbon to form WB + WC. This appears doubtful in the light of the present experiments, at least as long as a similarity between the behavior of tungsten and molybdenum is assumed. It is likely that some oxidation occurred in Brewer's experiments, so that boron was lost and that the remaining wolfram metal carburized afterwards. This reaction has been observed with molybdenum-borides. If oxygen was excluded, Mo$_2$B was stable and no carbide formed.

The existence of phase transformations in borides seems to be not uncommon, and it might be worthwhile to investigate some other borides at higher temperatures. Hansen[4] indicates phase changes in the Fe-B and Ni-B systems, though no high temperature structures are discussed. FeB is isomorphous with Mo$_2$B, but FeB has at room temperature a structure which is different from both MoB and CrB. If a high temperature form should exist, it would be interesting to find out whether it agrees with one of the other monoboride structures. Nothing is known about the structure of NiB. In the W-B system, a high temperature modification, isomorphous with β-MoB and CrB, has been reported.[5] CrB seems to be stable up to the melting point.

The tendency of the boron atoms to form bonds with each other is very strong, so that a loosening of the lattice by heating brings about a reshuffling of the boron atoms. Kiessling[6] has shown how closely related all the structures of the transition metal borides are for the same boron content. A systematic comparison of the boride phases of the transition metals of the 4th, 5th, and 6th groups of the Periodic System will, therefore, only be possible when the phase diagrams of these systems are studied in detail, and especially in the higher temperature regions.

Table II. Properties of Molybdenum Borides

Boride	Microhardness VPN 5-g per Sq Mm	Resistivity Microhm-cm
Mo_2B	2360	40
MoB	2500	45
β-MoB	2300	25
MoB_2	2300	25
MoB_4	1200	45

Properties of Molybdenum-Borides

Some physical properties of the molybdenum-borides were studied on small samples prepared by hot-pressing. About 8 to 10 g of powder were heated in small graphite dies to temperatures up to 1900°C and compressed while hot between graphite punches. The densities which could be obtained with these samples were often not very high, about 65 to 90 pct of the theoretical density, but these samples were satisfactory for a number of tests.

All borides are metallic; they can be polished to show metallic luster and are good conductors of heat and electricity. They are very hard and rather brittle. The modulus of rupture in transverse bending ranged between 25,000 and 50,000 psi, and the hardness was about 90 on the Rockwell A scale. They are, therefore, comparable with the hardest carbides. Attempts to distinguish between different molybdenum-borides by microhardness measurements did not produce conclusive results. Measurements with 50 g load are included in Table II, but it is doubtful whether MoB really is softer than the other borides. Errors arise from the difficulties in polishing, where grains are easily ripped out.

The electrical resistivity could be determined with better accuracy. Values obtained from samples of different densities could be extrapolated to 100 pct density and, in this way, more reliable data were obtained. Such an extrapolation is shown in Fig. 5. Fast cooled samples give the curve for MoB$_2$, while

slowly cooled or annealed samples result in values for Mo_2B; the difference between the resistivities of these two structures is easily seen. Resistivity values for all measured phases are included in Table II. It should be noted that the room temperature modification, Mo_2B, is a better conductor than its high temperature phase, MoB, while the reverse is true for the monoboride.

The rate of oxidation of the three room temperature boride structures was determined to check whether a higher boron content would retard or accelerate the corrosion at high temperature. Small samples were heated in still air, in a quartz tube, to 1000°C for various lengths of time, and the weight change was recorded. All samples lost weight rapidly, Fig. 6. Mo_2B was completely destroyed after 16 hr, while Mo_2B showed a loss of about 20 pct in weight after about 100 hr. MoB was between these two curves. A kind of glassy layer had formed on Mo_2B which obviously retarded the oxidation process. The difference in behavior of the three borides is quite remarkable, but none of them could be classified as oxidation resistant.

Acknowledgment

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Technical Note

Note on the Effect of Oxygen and Nitrogen on the Hardness and Lattice Parameter Of High Purity Vanadium

by S. Beatty

RECENT experimental results on the superconductive properties of vanadium indicate that the magnetic behavior of the metal is greatly affected by internal strains caused by mechanical work, and particularly by oxygen and nitrogen impurities. These result in an increase in the hardness of the metal such that metallurgists[1] have used hardness as a measure of the impurities. An increase in the impurities should also be reflected in a change of lattice parameter with increasing impurity content.

The lattice parameter of vanadium prepared by the thermal decomposition of the iodide has been determined by two workers. Neuburger[2] obtained a value of $a_o = 3.0338 \pm 0.0003$A for the body-centered cubic lattice by means of the powder method. The work of Katelaar is referred to by van Arkel[3] in which a value of $a_o = 3.025$ is given.

Four samples were used for this investigation. Sample A, the vanadium of the highest purity in the group, was obtained by means of the thermal decomposition of vanadium diiodide and deposited on a 3 mil diam tungsten filament in the form of crystals. The second sample, labeled B, was obtained by the calcium reduction of the pentaoxide at a sufficiently high temperature to give a melt. A third sample, C, was obtained in the same manner as B but remelted in a pure argon atmosphere. The last sample, D, was prepared by the calcium reduction method and the fine powdered vanadium was then sintered by means of applied heat and pressure. Samples A, B, and C were thus essentially free of mechanical strain in their preparation. Sample D was annealed in a high vacuum at 800°C.

The samples were prepared for X-ray diffraction analysis such that all additional strain by cold work or by contamination with oxygen and nitrogen was kept at a minimum. Powder obtained from filings was deemed unsuitable since this would require annealing to get rid of the cold work. A heat treatment up to 1000°C at 10^{-5} mm pressure might still increase the impurity content by means of adsorbed oxygen from residual gas in the vacuum chamber. The most satisfactory samples were prepared for back-reflection film techniques. Samples were cut to size, etched with hydrobromic acid, and mounted in Bakelite. They were then lightly polished on 3-0 paper and lightly etched.

Chemical and Hardness Analysis of Samples

Spectrographic analyses were made of the four samples and indicated similar metallic impurities for the group. The major metallic impurity in each sample was iron, which was less than 0.01 pct. The sum of the other metallic impurities was approximately 0.1 pct. The carbon content was assumed low by virtue of the methods of sample preparation. The principal impurity difference between the samples was in the oxygen and nitrogen content.

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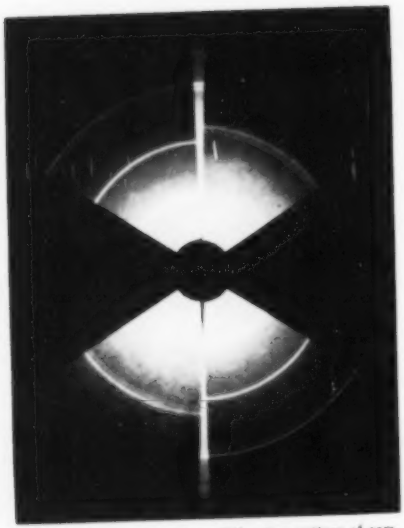

Fig. 1—Back reflection X ray diffraction pattern of sample A and silicon standard. Unfiltered radiation.

The oxygen content was determined by means of the vacuum fusion method; the nitrogen content by the Kjeldahl method.

Hardness measurements were made using a 1 kg load and a "Tukon" tester, a description of which has been given.[7] The values for the oxygen and nitrogen content, and hardness are given in Table I.

Experimental Procedure and Results

Back-reflection Laue photographs of the faces of several crystals of sample A showed the characteristic four-fold symmetry for the (100) plane.

A small crystal (100) face having a relatively flat surface was mounted in wax for Geiger counter spectrometer study to check the diffraction line contour. A very sharp pattern was obtained for the α_1 and α_2 reflections of the (200) plane at 61° 2θ using copper radiation.

For back-reflection study, the metallographically prepared smooth sample surface was mounted against a polished flat and held tight by means of a rear spring. On each film a pattern was obtained of the sample and of the smooth powdered silicon standard, mounted in Lucite and distributed by Norelco. The diaphragm was externally mounted to the film cassette to obviate removal between successive exposures. A back-reflection film of sample A is seen in Fig. 1 showing a sharp α_1 and α_2 line.

The lattice parameter was determined from the (321) reflection for the body-centered cubic structure and calibrated against the (533) and (444) reflections of the silicon standard. The values for the α_1 and α_2 lines for CuK radiation are 68.446°, 68.811° and 79.314°, 80.100°, respectively, for the standard. In this manner systematic error such as film shrinkage and approximate specimen-film distances were eliminated. The lattice parameter was determined from 10 films of 3 different samples. These gave a value of $a_o = 3.0282 \pm 0.0001$A at 30°C for this particular sample. The probable error of a single observation in this group is 0.0005A using conventional statistical methods. Samples B, C, and D were prepared in a similar manner and studied relative to sample A.

Table I. Oxygen and Nitrogen Content and Hardness of the Vanadium Samples

Sample	Hardness	Oxygen, Wt Pct	Nitrogen, Wt Pct
A	65 ± 10	0.038	0.021
B	115 ± 5	0.044	0.032
C	165 ± 5	0.075	0.106
D	245 ± 10	0.15	0.189

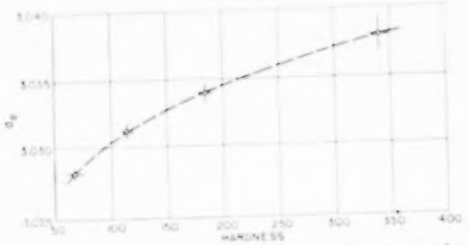

Fig. 2—Relationship between hardness and lattice parameter for vanadium.

An increase in lattice parameter was observed for samples with increasing oxygen and nitrogen content, and the observed curve for parameter vs. hardness is shown in Fig. 2. A similar effect has been observed for titanium.[8,9]

These parameters apply specifically to the four samples studied, but the trend appears significant. In order to extrapolate for the parameter of the pure metal, however, it would be necessary to study vanadium samples obtained from the iodide in which the oxygen and nitrogen content were controlled.

In addition to the parameter increase, a marked increase in line broadening was observed as the impurities increased. This can be attributed to nonuniform composition. The broadening was observed for a number of lines in addition to the (321) plane using a Geiger counter spectrometer. It appears to be characteristic of the spectrum as a whole rather than due to a tetragonal modification of the lattice, although precise powder patterns are required to substantiate this view. With the spectrometer, it is not possible to resolve the α_1 and α_2 reflections at 145° 2θ for sample D, while sample C showed overlapping. The contours for sample B were slightly wide.

Summary

Small additions of oxygen and nitrogen result in a sharp increase in the lattice parameter and hardness of vanadium.

Progressive line broadening is observed with increasing impurities content. This broadening appears due to nonuniform composition.

The samples were obtained through the courtesy of A. Wexler.

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AIME OFFICERS

President—

Vice Presidents—

President Elect and Treasurer—

AIME STAFF

Secretary—

Ass't. Secretaries—

Ass't. Treasurer—

aime NEWS

93 Pct of Voters Favor Continuing Present Dues

When the dues were increased by $5 for Members and Associate Members and by $2 for Junior Members in 1950 it was agreed that they would revert to the former level in 1953 unless the Board, supported by an affirmative vote of the voting membership, decided otherwise. It was believed in 1949 that the value of the dollar might cease to decline and that other factors might make it possible to revert to the former dues scale. But even at the higher rate the AIME had only a small surplus, $8009, in 1951, and a surplus slightly less than this is indicated for 1952, so continuance of the present scale seemed a necessity unless services to members were to be seriously curtailed.

Fortunately the AIME members agreed with this point of view, the final vote reported by the tellers being as follows:

	Number	Pct
Total ballots mailed	14,128	100
Total ballots returned	8,592	60.8
Valid ballots returned	8,513	60.2
Total yes vote	7,916	56.0

	Yes	No	Pct Yes
Mining branch	3349	239	93.0
Metals Branch	2114	128	94.3
Petroleum Branch	2127	202	91.3
No Branch specified	326	28	92.1
Total and average	7916	597	93.0

With this authority the Board will vote at its meeting on September 7 to change the bylaws to effect a continuance in the present scale of dues.

Directory to be Issued With December Journals

Present plans are to issue the new AIME Directory free to members with the December issues of the Institute's journals. It will be a complete Directory, except for the material already published in the Directory supplement issued with the June issues of the journals and the annual reports released last February and available in mimeographed form. That is, it will include the data previously published in the 1948 Directory on endowment funds, medals and awards, joint activities, constitution and bylaws, and necrology. The information on members will be based on the returned cards that were mailed to all members last spring, and unlike previous Directories will show the Divisional and Branch affiliations of members. The geographical section of the Directory will revert to the form used in the 1948 and previous Directories, rather than by companies.

C. R. Fondersmith, Chairman, National Open Hearth Steel Committee 1948 to 1949, is presented with an electric clock on behalf of the NOHSC, by Leo Reinartz, AIME President Elect for 1953. When the awards to Past Chairmen of the conference were made in April, Mr. Fondersmith was unable to attend. Present during this informal ceremony on July 8 were Edgar Westfall, Leo Reinartz, Charlie Staley, C. R. Fondersmith, Vernon Jones, and William Bergman.

M. Haider and E. Robie Plan Travel Itineraries

President Haider and Secretary Robie plan to attend the Fall Meeting of the Institute at Chicago, September 3 to 7, headquarters at the Palmer House. They will also both attend the Houston meeting of the Petroleum Branch, October 1 to 3. Secretary Robie has tentative plans to visit members and Local Sections in the following areas immediately following the Chicago meeting; September 8, Milwaukee; 9, Ishpeming and Houghton; 10, Ironwood and Duluth; 11, Hibbing; 12, Grand Forks; 16, Spokane and Coeur d'Alene; 17, Butte; 19, Laramie; 20 to 24, Denver. The President and Secretary expect to be in Pittsburgh November 7, and to visit the Carlsbad Potash Section on December 4, El Paso Metals Section, December 5, Southwestern New Mexico Section, December 6, and Arizona Section, Tucson, December 8.

MIED to Administer Petroleum Scholarship

Decision has been made to have the Executive Committee of the Mineral Industry Education Div. administer the AIME—Socony-Vacuum scholarship in petroleum engineering for the coming school year. The executive committee of the Division will adopt a permanent procedure for the administration of this and similar scholarships at its annual meeting in Los Angeles.

Hoover Medal Awarded

Clarence D. Howe will receive the Hoover Medal for 1952 at the Centennial luncheon in Chicago, September 10. Mr. Howe, a native of Massachusetts and an MIT graduate, has distinguished himself in Canada as a civil engineer and as a key member of the Ottawa Government.

Annual Meeting Paper Deadline

Sept. 15, 1952 is the deadline for all Institute of Metals Div. papers for the 1953 Los Angeles Annual Meeting and the deadline for all Iron and Steel Div., and Extractive Metallurgy Div. papers to be prepublished.

Personals

J. D. SWAIN

E. H. MANGAN

J. D. Swain and **E. H. Mangan** have been appointed executive vice-presidents of Electro Metallurgical Co., a division of Union Carbide & Carbon Corp.

Edmond L. Whittenberger has accepted a position with the U. S. Steel Co., Chicago.

Charles H. Gorski is now metallurgist for the E. I. duPont deNemours & Co., Inc., Baltimore. He had been with the pigments dept.

Frank D. Rosenthal is a metallurgist with the Frankford Arsenal, Philadelphia.

Charles D. Graham is with the General Electric Research Laboratory, the Knolls, as a student assistant.

Frank J. McEntee, the Western Precipitation Corp., has been transferred to the New York office.

Charles Peck is now located in Toledo for the Doehler-Jarvis Corp.

Raymond H. Hays formerly with the Caterpillar Tractor Co., Peoria, Ill. has accepted a position with the Ingersoll Products div., Borg-Warner Corp., Chicago.

A. P. Miller has joined the Newport Steel Corp., Newport, Ky. He formerly had been with the Inland Steel Co., East Chicago, Ind.

George P. Krumlauf has been made chief metallurgist for the Hamilton Foundry & Machine Co., Hamilton, Ohio. He had been foundry metallurgist for the Allen's Foundry & Machine Works, Lancaster.

Glen W. Wensch is no longer associated with the Fansteel Metallurgical Corp., North Chicago. He has become deputy chief, reactor materials branch, Savannah River operations office, AEC, Wilmington.

E. G. Bailey, founder and president of the Bailey Meter Co. and director and consultant of Babcock & Wilcox Co., was presented with the distinguished service award of Ohio State University.

Robert Austin, formerly with Consolidated Engineering Corp., Pasadena, has joined Beckman Instruments, South Pasadena.

Robert S. Burns has been appointed president of the Western Electrochemical Co., Culver City, Calif. **Kenneth Walsh** has been elected chairman of the executive committee.

George McCuskey has become assistant to the president, the Youngstown Sheet & Tube Co., Youngstown.

R. S. Stevenson was elected executive vice-president, Allis-Chalmers Mfg. Co., Milwaukee.

George Robinson recently joined the staff of Arthur D. Little, Inc., Cambridge.

J. O. Tompkins has been appointed assistant chief metallurgist, Keystone Steel & Wire Co., Peoria. **Harold Fales** has been named wire mill metallurgist.

Karl C. Ruppenthall has been named technical supervisor of the newly formed fine chemicals div., Pittsburgh Coke & Chemical Co., Pittsburgh.

Frank B. McKown was appointed vice-president of Kennecott Sales Corp., New York.

C. J. Plisky has been appointed vice-president in charge of production for the Pressed Steel Car Co., Inc., Pittsburgh. He had been vice-president in charge of the Unicel and Jahn trailer div.

Thomas J. Menzel is now plating chemist for the Hanson-Van Winkle-Munning Co., Matawan, N. J.

Herbert B. Jeffrey was promoted to assistant vice-president and assistant treasurer, Great Lakes Steel Corp., Detroit.

Edward A. Hassan, Jr., has been appointed manager, raw materials dept., Kaiser Aluminum & Chemical Corp., Oakland.

Arthur C. Bryan was appointed vice-president in charge of sales, National Carbon Co.

Howard B. Steggal, a vice-president, U. S. Radiator Corp., Detroit, was appointed senior vice-president.

A. E. Giblin was appointed works manager of Colorado Fuel & Iron Corp., Wickwire-Spencer steel div., Buffalo. He previously had been assistant plant manager of the Buffalo steel mills.

George B. Michie has been appointed vice-president of trade relations by the Electro-Refractories & Abrasives Corp., Buffalo.

George L. Dow is now associated with the Blaw Knox Construction Co., Pittsburgh.

Donald J. Barrett has been made turn superintendent, tin mill annealing, U. S. Steel Corp., Fairless works, Morrisville, Pa.

D. W. Watters, Dow Chemical Co., has been transferred to Madison, Ill. as production manager. He had been located in Midland, Mich.

Pol G. Boel is now assistant to the president, Usines Gustave Boel, La Louviere, Belgium.

Jaydee I. Dodson has joined the Pacific Northwest Alloys, Spokane. He had been associated with the U. S. Steel Co.

Guy Bridgstock has resigned from the Hudson Bay Mining & Smelting Co. to accept the position of plant metallurgist for the Canadian Copper Refiners Ltd., Montreal.

GUY BRIDGSTOCK

Gordon Erspamer is metallurgical engineer for Battelle Memorial Institute, Columbus.

Arthur Beyer, Jr. has accepted a position with the Atomic Energy Commission, New York.

Charles L. Ficker, plant superintendent, U. S. Steel products div., Los Angeles, has been appointed vice-president, operations, of the div. with headquarters in New York.

Raymond T. Whitzel has been named general manager of the smelting div., Aluminum Co. of America, succeeding **V. C. Doerschuk.** Mr. Doerschuk has been made technical consultant, chiefly on aluminum smelting and related problems.

P. M. Buhrer and **C. O. Kleinsmith** have been appointed executive vice-presidents of National Carbon Co., a div. of Union Carbide & Carbon Corp.

Alvin Jacobs is now employed as a research engineer by Battelle Memorial Institute.

J. W. Fredrickson has become metallurgist for the Dow Chemical Co., Midland.

Max I. Beard has joined the Oliver Corp., South Bend, Inc., as plant metallurgist.

Douglas Bourke is now project manager for the General Engineering Co., Ltd., Potosi, Mo.

Alex Briber has accepted a position with the McNally Pittsburg Mfg. Corp., Pittsburg, Kan.

H. Curtis Barber is now with E. I. duPont deNemours & Co., Inc., Wilmington, Del.

Lawrence C. Flickinger has been made chief chemist for the Youngstown Sheet & Tube Co., Youngstown.

W. P. Morris has joined the Combined Metals Reduction Co., Salt Lake City. He had formerly been associated with the Oliver Iron Mining Co., Virginia, Minn.

W. P. MORRIS

Rafford L. Faulkner is now assistant to the director, div. of raw materials, AEC, Washington, D. C.

C. Ernest Birchenall has joined the staff of Princeton University as associate professor of chemistry at the Forrestal Research Center, Princeton, N. J. He had been an assistant professor at the Carnegie Institute of Technology, Pittsburgh.

Dean N. Williams has accepted a position with the Kaiser Aluminum & Chemical Corp., Spokane, Wash.

Donald F. Haskell has joined the engineering dept. of the American Smelting & Refining Co., New York.

A. G. Wolf, manager of the geological dept., **C. O. Stephens,** manager, gas dept., and **H. W. Strickland,** assistant to president, have been named vice-presidents of the Freeport Sulphur Co.

Chester H. Steele has been appointed vice-president in charge of western operations, Anaconda Copper Mining Co.

Avelino I. de Oliveira is now general director of the Departmento Nacional de Producto Mineral, Rio de Janeiro, Brazil.

Harvey J. Hakala has accepted a position with the U. S. Steel Co., Rio de Janeiro.

A. S. Froes had been in the United States and recently returned to Rio de Janeiro where he is associated with the Instituto Nacional de Technologia.

E. G. Bailey and **H. S. Mudd** have been elected honorary members of the American Society of Civil Engineers.

M. E. Cieslicki is now associated with the General Electric Co., Lockland, Ohio.

J. S. Breitenstein, National Lead Co., has been transferred from South Amboy, N. J. to Cincinnati.

R. Campbell Williams has resigned as technical manager, New Metals & Chemicals Ltd., London. He is now engaged in private consulting, specializing in the rarer metals and alloys.

Yurii E. Lebedeff, superintendent of chemical metallurgy in the central research dept., American Smelting & Refining Co., was awarded the honorary degree of doctor of science at the South Dakota School of Mines and Technology.

W. P. Jones has been appointed general manager of the Chemical Construction (Inter-American) Ltd., Toronto, Canada. The company is a newly formed subsidiary of American Cyanamid Co.

Lawrence Litchfield, Jr. has been elected president of the Alcoa Mining Co., New York, and Surinaamsche Bauxite Maatschappij, Suriname. He succeeds **Frank B. Cuff** who has retired.

Donald N. Frey is now manager, metallurgy dept., scientific laboratories, Ford Motor Co., Dearborn.

Bernard J. Alperin has joined the General Electric Co., Erie, Pa., as melting foreman.

Campbell W. Funk is now with the Aerojet Engineering Corp., Azusa, Calif.

Robert C. Good, Jr., formerly physicist at Lehigh University, is now research physicist for the Franklin Institute, Philadelphia.

H. J. Hamjian is now in the research dept., Utica Drop Forge & Tool Corp., Clayville, N. Y.

John D. Alstetter has become associated with the Ford Motor Co., manufacturing research div., Dearborn.

Frank A. Crossley is associate metallurgist with the Armour Research Foundation, Chicago.

Gordon R. Baer has joined the Freyn Engineering div., Koppers Co., Chicago.

Robert L. Garrett has accepted a position with the Aluminum Co. of America, Cleveland.

Leslie W. Pullen is now design engineer for the Western-Knapp Engineering Co., Corydon, Ind.

Obituaries

Wallace Charles Devereux (Member 1937), managing director of Almin Ltd., England, died on June 21. Col. Devereux was born on Mar. 9, 1893. He was educated at King Edward's Grammar School. During the first world war he was superintendent of the National Aircraft Factory No. 1. In 1927 he founded High Duty Alloys Ltd. to carry out research and development leading to the commercial production of the new high strength alloys needed by the aircraft industry. He was director of Light Alloy Forgings from 1939 to 1941. For one year he was controller of American Aircraft Supplies. In 1945 he founded Almin Ltd. (Associated Light Metal Industries). In addition to being managing director of Almin, Col. Devereux was a chairman and director in several other companies.

John S. Unger (Member 1891) died on May 15. Mr. Unger was retired manager of the central research bureau, U. S. Steel Co. (Carnegie-Illinois Steel Co.), Pittsburgh.

Marcus A. Grossman (Member 1920) died on May 21 after a long illness. Dr. Grossman was adviser-research planning for U. S. Steel Co., Pittsburgh. He was born at Youngstown, Ohio on Sept. 13, 1890 and graduated

M. A. GROSSMAN

from Massachusetts Institute of Technology (S.B.) in 1911. He joined the staff of MIT as an assistant instructor for one year and then became associated with the Pittsburgh Testing Laboratory. In 1915 he accepted the position of metallographer with the American Vanadium Co., Bridgeville, Pa. Dr. Grossman joined the Bureau of Standards, Washington, D. C. in 1917 and returned to American Vanadium in 1919. He became chief metallurgist for the Electric Alloy Steel Corp., Canton. He then joined the United Alloy Co., which became part of Republic Steel Corp. In 1926 he was chief metallurgist for the Central Alloy Steel Corp. and in 1931 joined the Illinois Steel Co., which later became the Carnegie-Illinois Steel Corp. Dr. Grossman received his Ph.D. from Harvard in 1931. He was a past president of the American Society for Metals and the recipient of the Albert Sauveur Achievement Award of the ASM at the National Metal Congress in 1949. He was also a Campbell Lecturer and Howe Medalist. Dr. Grossman authored two books on heat treatment and hardenability.

William J. Menke (Member 1928) died on April 24. Born at Pittsburgh, he received his A.B. degree from the University of Michigan. In 1923 Mr. Menke joined the Youngstown Boiler & Tank Co., as inspector, plates and finished material. He became associated with the Shenango Furnace Co. as assistant superintendent blast furnaces. In 1927 Mr. Menke was promoted to assistant superintendent, foundry. At the time of his death he had been general superintendent of blast furnace, and also of the ingot mold foundries of the Shenango-Penn Mold Co.

John Rice (Member 1892), founder and honorary chairman of the board, General Crushed Stone Co., Easton, Pa., died on May 22. Mr. Rice was born in 1866 and graduated from Yale University.

Vaclav Gregor (Member 1938) died on Apr. 30. Born in Bohemia in 1887, Mr. Gregor attended the Universities of Prag and Berlin. After graduation he joined the Komorau Eisenwerke, Komorau, Bohemia, as openhearth engineer. He came to the United States and joined the Carnegie-Illinois Steel Co., Gary works as practice engineer. He was made mechanical engineer, open hearth; assistant to div. superintendent of open hearth and central rolling mills; superintendent, fuel dept., respectively; and at the time of his death was assistant superintendent of steel production.

Clark White (Member 1944) retired metallurgical engineer, died of a heart attack at Ashland, Ky. Mr. White was born June 14, 1882 at Scottdale, Pa. In 1899 he was employed as a machinist and chief engineer for Dunbar Furnace Co., Dunbar, Pa. For four years he was shops superintendent for the W. J. Rainey Coke Co., Uniontown, Pa. and in 1914 joined the Columbus Iron & Steel Co., Columbus, Ohio. He was made blast furnace superintendent for the American Manganese Mfg. Co., Dunbar in 1917 and in 1923 joined the American Rolling Mill Co., as superintendent. From 1930 to 1944 he owned and operated the Ashland Brick Co., Summit, and was with the Pittsburgh Metallurgical Co. from 1944 until he retired in 1949.

Gerald J. Weckmueller (Member 1945) formerly assistant superintendent, blast furnaces, Inland Steel Co., East Chicago, Ind., died on June 4. Born in Milwaukee, Mr. Weckmueller graduated from the University of Wisconsin with the degree of B.S. in 1932. He worked at the south works of the U. S. Steel Co. (Carnegie-Illinois Steel Co.) from 1933 to 1941. In 1941 he joined Inland Steel Co. He had been associated with the Blast Furnace & Coke Assn., Chicago district. At the time of his death, Mr. Weckmueller was residing at Whiting, Ind.

Leonard Aldridge (Member 1942) died in Italy on June 8. Mr. Aldridge was born at London in 1892. He had interests in collieries in England and South Africa as well as iron ore mines in France and Norway. He also had financial investments in manganese deposits in South Africa and controlling interests in engineering works in Birmingham and South Africa. His residence was in London.

NECROLOGY

Date Elected	Name	Date of Death
1942	Leonard Aldridge	June 8, 1952
1949	Virgil D. Basinger	Unknown
1946	W. R. Benedict	July 9, 1952
1916	Andrew B. Crichton	July 9, 1952
1949	Vernon J. Nelson	May 31, 1952
1947	John C. Reed	June 14, 1952
1919	Hugh M. Shepard	May 30, 1952

Proposed for Membership — Metals Branch AIME —

Total AIME membership on July 31, 1952 was 14,077; in addition 1346 Student Affiliates were enrolled.

ADMISSIONS COMMITTEE

T. H. Jones, Chairman, Thomas G. Moore, Vice-Chairman, Harold S. Bell, F. W. Hanson, R. H. Chadwick, T. W. Nelson, J. R. Seal, John T. Sherman, A. C. Booker, John Lyons, C. A. R. Lundin, G. P. Larson, F. A. Firmin, and C. Lorne Rice, Jr.

The Institute desires to extend its privileges to more people to whom it can be of service, but does not desire as members persons who are unqualified. Therefore members are urged to serve this end as soon as possible by considering candidates for admission and membership to inform the Secretary's office if names of people are known who are known to be unqualified for AIME membership.

In the following list C.S. means change of status, R. reinstatement, M. Member, J. Junior, A. Associate Member, S. Student Associate.

Connecticut
Hartford—Petsch, Herman F. (A)

Illinois
Western Springs—Brown, Frank E. (M)

Maryland
Takoma Park—Kurtz, Horace F., Jr. (R.C.S.—S.J.)

Michigan
Detroit—Holmes, Richard W. (J)

New Jersey
Elizabeth—Nuetzel, Cyrus S. (M) (C.S.—A.M.)
Haddonfield—South, Frank E. (A)
Princeton—Semmel, John W., Jr. (J) (C.S.—S.J.)

New Mexico
Vanadium—Tomonea, Donald R. (M)

New York
Grand Island—Fulkman, Robert L. (J) (R.C.S.—S.J.)
Schenectady—Bianchi, Leonard M. (J) (R.C.S.—S.J.)
Tuckahoe—Sullivan, John W. W. (M) (R.C.S.—A.M.)

Ohio
Columbus—Goodwin, Harry B. (M) (R.C.S.—S.M.)

Oregon
Troutdale—Kibbe, Robert M. (M)

Pennsylvania
Pittsburgh—Cummings, William G., Jr. (J)
Pittsburgh—Mercer, George E. (A)

Texas
Fort Worth—Phelps, Harold E., Jr. (M)

Utah
Tooele—Keene, Milton LaV. (J) (R.C.S.—S.J.)

Washington
Vancouver—Yeasley, John W. (A)

Argentina
El Aguilar—Milan, Jose (J)

Australia
Marble Bar—Grae, Francis E. (J)

Canada
Britannia Beach, B.C.—Jokisch, Carl R. (J) (R.C.S.—S.J.)
Kingston, Ont.—Gibbons, Donald F. (J)
Rossland, B.C.—Peters, Ernest (J) (R.C.S.—S.J.)
Trail, B.C.—Piper, Lawrence S. (M)

Finland
Helsinki—Tikkanen, Matti H. (M)

Italy
L'Aquila—Koch, Renato (M)

Japan
Tokyo—Fujiwara, Tadayoshi (M)

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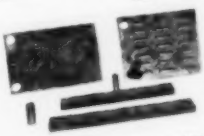

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